REMOVAL OF CALCIUM ION FROM SUGAR SOLUTION THROUGH ELECTRODIALYSIS

A Thesis Submitted

in Partial Fulfilment of

the Requirements for the Award of the Degree of

MASTER OF TECHNOLOGY

by

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to the

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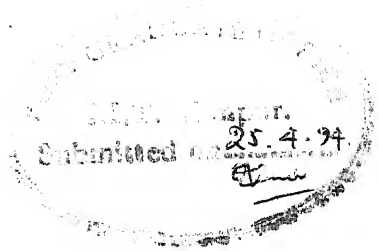

CERTIFICATE

It is certified that the present work entitled **Removal of Calcium Ion from Sugar Solution Through Electrodialysis** *has been carried out by* Sujay Chattopadhyay *under my supervision and that it has not been submitted elsewhere for a degree.*

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Abstract

The efficacy of electrodialysis in the removal of micro-ions like Ca^{2+} from aqueous solutions (of sugar) has been studied. Experiments were performed in a continuous electrodialyzer having three compartments under both co-current and counter-current flow conditions. The effect of various operating conditions *eg* concentration in feed, cation Ca^{2+} concentration in the feed, applied electrical potential across the membranes (voltage), types of membranes used (Cation-Anion Configuration), pH of the catholyte and anolyte, flow rates of the catholyte, anolyte and the feed solution, *etc.*, on the removal of Ca^{2+} ions, were studied. Based on these studies, the most suitable range of operation is determined. It is observed that a catholyte consisting of EDTA and AA in aqueous medium is able to avoid fouling of CEM on the catholyte side. A reasonably high percent removal of Ca^{2+} ion around 85 percent was achieved under these conditions. Results based on regression analysis studies indicate that Electrodialysis is an effective method for the removal of Ca^{2+} ions from sucrose solutions.

Acknowledgement

In retrospect, I realize that one of the most important decisions I made was the choice of my research advisor. I want to express my deep gratitude, respectful regards and sincere thanks to Prof. P. K. Bhattacharya for his constant encouragement and discerning guidance throughout the course of my research work.

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Sujay Chattopadhyay

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Nomenclature

A	Anolyte
AW	Acid wash with 0.1 M HCl
C	Catholyte
C_+	Concentration of the cation in the bulk
$\bar{C}_+$	Concentration of the cation on membrane surface
$\bar{C}_-$	Concentration of the anion on the membrane surface
C_{AA}	Catholyte acetic acid concentration (mol/l)
C_{Ca}	Calcium concentration in feed (mol/l)
C_{EDTA}	Catholyte EDTA concentration (mol/l)
F	Feed
I	Current (amp.)
Q_{CA}	Catholyte and Anolyte flow rate (ml/min)
Q_F	Feed flow rate (ml/min)
R	Percent of Calcium removed
t	Time (min)
V	Applied voltage (V)
W	Distilled Water
λ	Conductivity (mMho)
α	Constant defined in eqn.(4.2)
β	Constant defined in eqn.(4.2)
γ_+	Activity coefficient of the cation
γ_-	Activity coefficient of the anion
$\bar{\gamma}_+$	Activity coefficient of the cation on the membrane surface
$\bar{\gamma}_-$	Activity coefficient of the anion on the membrane surface

Abbreviations

AA	Acetic acid
AEM	Anion Exchange Membrane
CEM	Cation Exchange Membrane
ED	Electrodialysis
EDTA	Ethylene Diamine Tetra Acetic acid (di-sodium salt)
f	Fouling observed
nf	No Fouling
RN	Run Number

Chapter 1

Introduction

The sugar industry is an important agro-industry. The sugar cane contains not only sucrose but also numerous other dissolved substances, as well as cellulose or woody fibre. Constituents of ripe cane vary widely in different countries and regions but fall generally within a certain limit [1], as shown in Table 1.1. Other organic matter includes proteins, organic acids (glycollic, malic and succinic, etc.), pentosans and pectins (gums), colouring matter and wax. Inorganic matter includes anions of phosphates, chlorides, sulphates, nitrates and silicates along with cations like sodium, potassium, magnesium, aluminium and iron. The nitrogenous bodies are albuminoids, amides, amino acids, ammonia and xanthene bases.

The juice obtained from cane is an opaque liquid whose colour varies from grey to dark green; probably due to the presence of chlorophyll, anthocyanin, saccharetin and tannins [1].

Conventionally, the cane juice is clarified to obtain pure crystallized sugar. The clarification of raw cane juice is done for two purposes:

1. Removal of impurities:
   (*a*) To precipitate dissolved inorganic non-sugars present in the juice in colloidal state thereby to increase the percentage of available or crystallizable sugar.
   (*b*) To separate insoluble solid matters suspended in juice in colloidal state rendering the juice opaque, viscous and dark in colour. These impurities can not be separated by simple filtration of the raw juice but are separated along with non sugars precipitated by the action of heat, leaving the juice transparent.
2. Bleaching effects:

   After the impurities are removed by chemical treatment of the juice, bleaching is carried out to make the juice light in colour as it is necessary for the manufacture of white sugar.

The clarifying agents that are used in the chemical treatment of cane juice for the manufacture of plantation white consumption sugar are [1]

(*a*) Lime,

(*b*) Phosphoric acid or its compounds,

(*c*) Sulphur dioxide, and

(*d*) Carbon dioxide.

Essential requirements for good clarification are as follows:

(*a*) Sucrose should remain intact during clarification.

(*b*) Reducing sugars are neither formed afresh nor destroyed during chemical treatment.

(*c*) Molasses formation should be low.

(*d*) The lime content in the clarified juice must be as low as possible.

An optimum clarification can be attained through the application of the following principle:

Optimum quantity of lime is used as required in each system of clarification at proper 'pH' and 'temperature'[1].

After proper clarification and heating, the impurities in the cane juice form lump and precipitate. This is then removed either by filtration or decantation. The clear clarified juice is concentrated to a syrup of about 60 brix (conventional unit in which sucrose solution concentrations are measured in sugar industries [1]) in multiple-effect evaporators. In the second stage, the thick syrup is further concentrated to a "massecuite", of 93 to 100 brix in a vacuum pan. This processes is called 'boiling to grains' and finally crystallization takes place. This leads to the formation of crystallized white sugar grains leaving a thick syrup (mother liquor) called molasses [1]. A block diagram of an industrial sugar production process is shown in fig. 1.1.

Addition of lime(liming), during the clarification stage introduces metal ions mainly Ca^{2+} in the clarified cane juice. Disadvantages caused by the presence of excess calcium or other alkaline earth metal ions and some heavy metal ions like iron, aluminium etc., are:

(*a*) Scale formation in the evaporators.

(*b*) Improper crystallization.

(*c*) Molasses percentage may increase due to inversion of sucrose in alkaline medium.

(*d*) Storage is hampered because of hygroscopic nature of these metals, associated with sugar.

(*e*) excess calcium is not hygienic. However clarification of the raw juice is necessary as the extent of this treatment determines the purity and quality of the product(sugar).

Keeping all the above shortcomings in mind, these alkaline earth metals should be moved effectively immediately before their entry into the evaporators. Conventional processes use optimum amount of lime to reduce the above stated disadvantages; however, some problems remain. A new interest has recently emerged considering application of membrane technology in the sugar industry. Membrane processes have the necessary ability to overcome many of the associated disadvantages of the conventional sugar processing. Some of the streams with potential membrane separation applications are [2]

. The clarification of raw juice after liming by ultrafiltration (UF).

. Treatment of thin juice after liming and heating by electrodialysis (ED).

. Treatment of thick juice after liming by ultrafiltration (UF).

. Treatment of molasses by ultrafiltration or electrodialysis.

. Treatment of raw sugar by ultrafiltration.

An attempt has been made to select the second stream and thus treat thin juice after liming by electrodialysis (ED). ED is an unit operation in which the ions are transported through a membrane with an electrical driving force. Chemical separations are obtained when the rates of transport of ions through the membrane differ from the rates in free solutions. The membrane may provide simple steric hindrance to the transport of different ions on the basis of their sizes, or it may be selective towards ions on the basis of the sign of their charge or density. Shigemasa, et.al. [3,4] have attempted to remove calcium ion from sugar solution by electrodialysis. They further carried out desalting and separation of mixed carbohydrates by ED with ion exchange membranes [5,6]. They observed good

relationships between the removal of calcium ion and the amount of electric current. The removal rate of calcium ion increased with an increase in the membrane area and the applied voltage [3,4]. Further, the work done by Shigemasa, et.al. [3-6] does not consider many of the possibilities which may enhance the rate of removal of calcium ion. More so, a systematic experimental study in this area was thought appropriate considering the importance of the industry.

The present work highlights the study of ED of a synthetic solution of 5% (around 5 brix) sucrose and a known amount of calcium chloride in distilled water. The objectives of the work are as follows:

1. To select the best possible system (simultaneously to observe and avoid the fouling of ion exchange membranes) for the removal of calcium ion, and,
2. To study the effect of various operating parameters of the selected system on the removal of Ca^{2+} ion.

Table 1.1

Components	Weight %	Weight % in dry basis
Water	72.0	—
Sucrose	12.0	42.8
Reducing sugars	1.3	4.6
Organic matter other than sugar	0.7	2.5
Inorganic matter	0.4	1.4
Nitrogenous bodies	0.7	2.5
Ash	0.6	2.3
Fibre	12.3	43.9

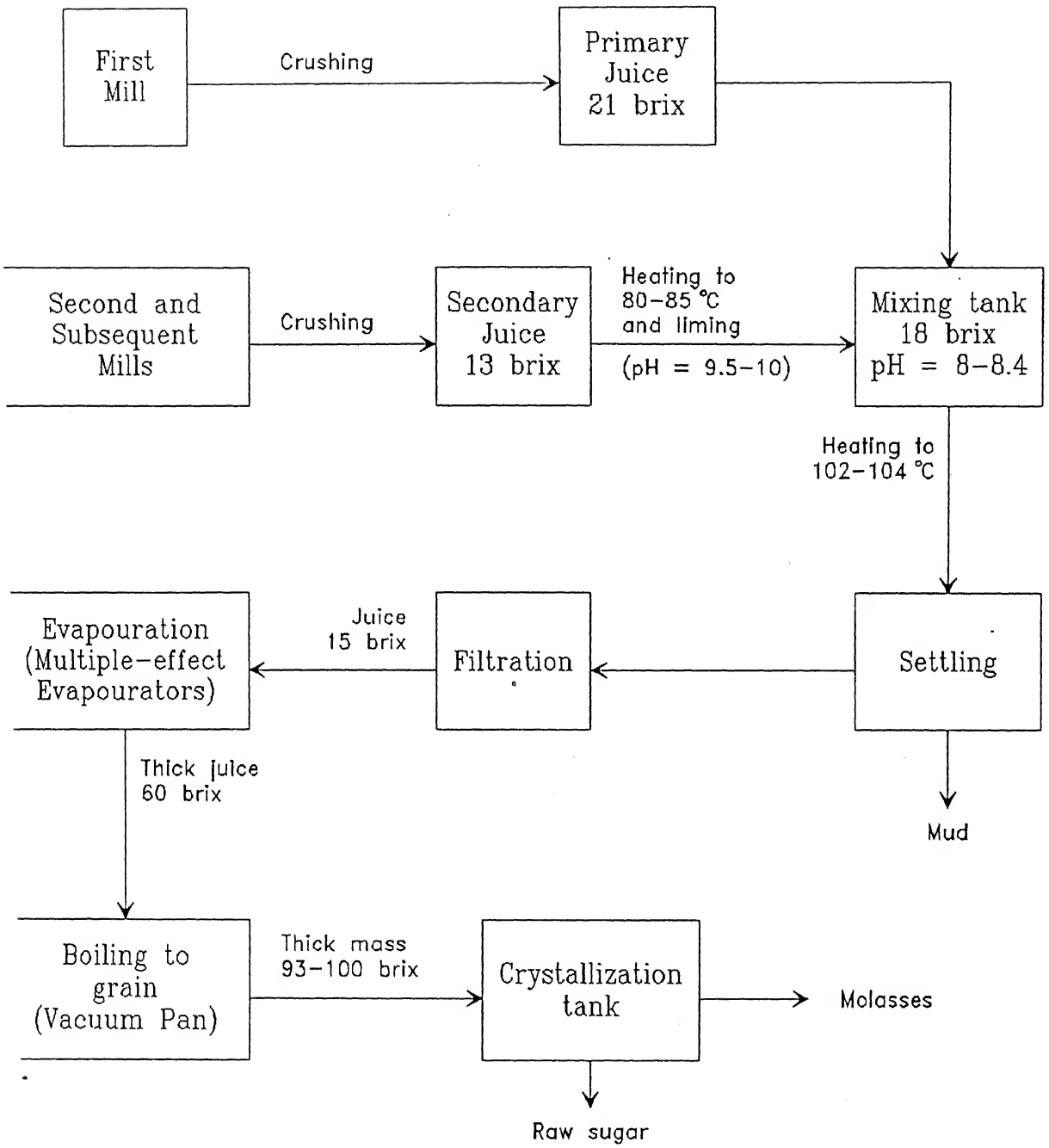


Fig 1.1 Simplified flow sheet of conventional sugar processing

Chapter 2

Literature Review

2.1 Fundamentals of Electrodialysis Operation

Electrodialysis is an unit operation using membranes in which partial separation of the components of an ionic solution is carried out by an electrical driving force. Electrodialysis may be classified along with solvent extraction and reverse osmosis (hyperfiltration) as a "selective transport" method. Here the salt or solvent is transported away from the feed solution through some physical barrier, with no change in state of any component in the system. Actually, the movement of the ions in the solution depends on its transport number (*i.e.*, the fraction of the total current carried by a particular ion in the solution). In this process, the dissociated ionic species move under the influence of an electrical potential towards an oppositely charged membrane and if the pore sizes are large enough for the species to pass through, they cross the membrane and are released at the other side as neutral species.

To maintain the electroneutrality condition, an equivalent amount of oppositely charged species should also move in the opposite direction and should be removed from that particular chamber. If an electrical driving force is applied, the respective ions will move towards oppositely charged electrode. Now to prevent the movement of the other ions (*i.e.*, which is counter with respect to a particular ion) a perfectly selective (with a particular ion) membrane is placed. The cation exchange membrane (CEM), *i.e.*, charged with negative ions, like bisulphite ion [HSO_3^{-1}], allows positive ions or cations to pass through. The anion exchange membrane (AEM), *i.e.*, charged with positive ions, like trimethyl amine [$N(CH_3)_3]^{+1}$, allows negative ions or anions to pass through.

2.2 Types of Electrodialysis Configuration

There can be at least six types of electrodialysis configurations [7] with various arrangements of ion exchange membranes. These are:

1. Single ion-exchange membrane ED
2. Neutral membrane ED
3. Cation-neutral membrane ED
4. Cation-anion membrane ED
5. Electrogravitation
6. Multicell single stage ED

2.3 Cation-Anion Exchange Membrane Electrodialysis

Various arrangements of cation and anion exchange membranes are used to avoid the difficulties of fouling at cation exchange or anion exchange membranes [8]. When an external electrical driving force is applied, the dissociated ions start moving towards the oppositely charged membranes where only one type of ions are allowed to pass through but the others are retained [9]. Thus, the solution put in between the two membranes gets depleted of the dissociated electrolyte and the catholyte and anolyte streams become richer in the respective ions.

In the ED process, ions pass through the membrane from the feed chamber to the membrane to the catholyte and anolyte side. It may so happen that the ions form a precipitation on the membrane surface. This precipitation causes an extra resistance to the ionic transport. This can be avoided by choosing a suitable reagent in catholyte and anolyte stream, which forms a stable complex with this foulant ion. This is called enhanced or activated transport in electrodialysis [8,9].

2.4 Concentration Polarization in Electrodialysis and Limiting Current Density

Concentration polarization is the most important phenomena which is to be taken into account in any membrane process. In any membrane separation process, larger species get accumulated on the membrane surface, forming a layer adjacent to the surface. This concentrated layer provides an extra resistance to the transport process. This phenomena is termed as concentration polarization [10]. This is deleterious to the membrane performance in terms of both flux and species transport through the membrane.

Due to this concentration variation across the membrane diffusion plays an important role and the ion transfer rate is actually an added effect of diffusion and ionic mobility. Under unfavourable condition it may so happen that the concentration may decrease to such a low value that no mineral ions are available for current transport any longer and then water dissociation starts. This actually results in either of the following effects [9]:

1. The pH level in the diluate side will fall.
2. The electrical resistance will increase.
3. The retentate pH will increase.
4. The current efficiency will drop.

At this condition, the current density attained is called Limiting Current density [9]. On further raising the applied voltage there will be no change in the cell current and therefore limiting current density denotes the upper limit of the current through the stack.

2.5 Mass Transfer in Electrodialysis

The ED process should be operated below the limiting current density [10,11] in order to conserve energy. Shaffer and Mintz [8] derived an expression for the voltage current curve using Nernst-Plank equation. However, the side effects (*i.e.*, water splitting, electro-osmosis etc.) were not taken into consideration in their analysis. Cowan and Brown [11] studied the effect of turbulence on limiting current in Electrodialysis cells. They observed that although polarization can be destroyed by turbulent flow, above a critical current density polarization is again noticeable.

Several studies have been done to incorporate the effects of mass transfer on efficiency of the process. Studies mainly involve effects of turbulence, flow configuration, co-current counter -current and cross flow, use of buffer or spaces, etc.

Barba and Evangelista [12] have found out an analytical method for designing and performance evaluation of co-current and counter-current electrodialysis stacks operated at high concentrations. Membrane area, concentrations and flow rates of the outlet streams are calculated explicitly. When the method is compared with numerical procedures, no significant discrepancies are found between the two.

Huang and You [13] have studied the effects of Reynolds number, Schmidt number, and geometry of the ED cell on the Nusselt number, in ion-exchange membrane electrodialysis. An empirical correlation under limiting current density condition was proposed:

$$\mathrm{Nu}_D = 1.793 \times (\mathrm{Re}^{0.34}) \times (\mathrm{Sc}^{0.329}) \times (de/L)^{0.301}$$

Considering Nernst Plank, Donnan, Poisson formalism and assuming the stated conditions, an 'S' shaped curve was obtained in current *vs* voltage plot and this was responsible for the different "side effects" (eg. water hydrolysis, pH variation, current efficiency change etc.). The different contributions of the electroneutrality condition, co-ion flux at the current *vs* curves and electro-osmotic flow on the total potential drop was estimated numerically [14].

2.6 Removal of ionic species from various feed streams using ED

Sugar cane juice contains ionic materials. These ionic materials decompose sucrose molecules, leading thereby increase of molasses formation. This is undesirable in the sugar industry. These ions can possibly be removed by ED. Tragardh and Gekas carried out mass transfer studies [2] of the removal of potassium ion. They suggested that, the main reason for the relatively high concentration of sucrose in cane molasses is due to ionic materials (*i.e.*,the ash) and the non-sugar organic material. These actually inhibit the crystallization of sucrose. If the concentrations of these materials were reduced, much of the sucrose could be recovered. They suggested that by applying ED to a diluted molasses feed (to reduce viscosity) separation would be possible which are:

(*a*) A concentrated solution containing potassium.

(*b*) A diluted ion-free solution containing the sugar.

Thin sugar solution mainly consists of the chlorides, sulphates, phosphates of sodium calcium magnesium and iron. Among these, calcium salts are in the maximum quantity. These calcium salts cause scaling of the evaporator which are used in the subsequent processing of the thin sugar juice. Hence, the removal of calcium ions is of utmost importance in sugar industry. Shigemasa *et. al.* [3,4] have worked on the removal rate of calcium ion which increases with the increase in the membrane area and the applied voltage. They have also studied the concentration of electrolytes, the counter ion of anion and cation-exchange membranes, the effect of stirring, and the boric acid concentration of the feed chamber on the removal of calcium from a sugar solution. This technique was also applied to the desalting of formose obtained from formaldehyde in the presence of base [3,4]. Despite stirring of the outer anolyte and catholyte compartment, the calcium ion transfer rate was almost the same as in the unstirred condition. But stirring the feed solution the calcium ion transfer rate was a little higher [4]. The removal rate of calcium is directly proportional to the membrane area and applied voltage [4]. Boric acid forms a complex with sugar [4] and under this condition calcium ions are removed by electrodialysis using ion exchange membranes.

Kumar *et. al.* [15] carried out electrodialysis on a semi-commercial scale for demineralizing clear sugar juice. According to them, removal of inorganic salts from clear juice will be of immense benefit to the process provided suitable membranes to withstand high temperature of clear juice was developed and cooling of clear juice is not required. This will reduce scaling in heat exchanger, reduces molasses formation and improve in sugar recovery.

Extensive research activities have also been undertaken in India to demineralise sugar cane juice by ED [16] . The scientists at CSMCRI, Bhavnagar, reported 4–6 units rise in purity of sugar cane juice along with 50–90% salt reduction [16].

Neytzell-de Wilde [17] carried out ED tests on distillery effluents after removal of suspended and undissolved matter. It was found that between 50–60% of potassium can be removed from the effluent at a current efficiency of about 50–55% and a D.C. power consumption of 0.75 to 0.85 KWh. per kilogram of potassium removed, provided the ED stack is operated at low voltage. Water transport also occurred together with transfer of some organic components.

Hirata and Tanaka [18] measured the ionic concentration within the membrane and membrane conductance in an amphoteric membrane and mixed-electrolyte system. The transport no. of calcium ion is larger than that of sodium ion in the whole concentration range and decreases with increasing concentration of the outer electrolyte solution. They also studies the heat transport numbers for a mixed electrolyte system and proposed thereby to predict the same. The transport numbers estimated were approximately in good agreement with the values obtained from ED experiments. Further, the transport numbers for two different ionic states in the membranes were evaluated and the concentration dependence of the total transport no., was discussed on the basis of these results.

Efforts have been directed in previous works to treat industrial effluents, namely, black liquor in ED. Mishra and Bhattacharya [19,20] observed that, both in the batch and continuous mode of ED a cation-neutral membrane gave a better percent caustic recovery than a neutral cellophane arrangement. The effect of current density on current efficiency and variation of the specific power consumption with percent caustic recovery also were

studied. It was also observed that the ED process can successfully be applied to recover various ionic species (mainly, Na^{1+}) from black liquor [21]. The present work is a continued study to apply ED as a potential technology for removal of ionic species from sugar solution. The objective of the present work is to determine the viability of the technology for food processing industries, particularly in the areas of purification of various process streams.

CHAPTER 3

Experimental Considerations

3.1 Materials and Instruments

3.1.1 Membranes

Properties	Values for CEM	Values for AEM
Transport number	0.91	0.90
Experimental resistance (ohm cm^{-2})	2.0-3.5	—
Maximum mechanical pressure allowed ($Kg.cm^{-2}$)	3.0	3.0
Thickness (mm)	0.11–0.15	0.09–0.11
Max. Temperature (°C)	60	60

3.1.2 Electrodialysis set up

Make Berghof (Germany) ED stack

Effective membrane area (cm^2):	37	Cell volume (cc):	7.4
Compartment thickness (mm):	2.0	Electrodes:	Graphite

3.1.3 Power supply unit

Mains connection voltage	110/220V A.C. 50-80 Hz.
Output voltage setting	0-49.9V D.C.
Output current setting	0-3.99AC

3.1.4 Pumps

Four centrifugal pumps with a capacity of 8 lit/min. in no load condition.

3.2 Conductivity Meter

Make	Systronics (India)
Conductivity range	200 mMho in 5 ranges
Measuring accuracy	Within ±1%
Indication	On digital panel meter
Power requirements	230V ±10% 50 Hz single phase, 6VA

3.3 Solutions

Feed, anolyte and catholyte were the three chambers in the electrodialysis cell. The feed chamber is in between the catholyte and anolyte chambers. Some important information used in the preliminary runs (run no.1 to 13) are:

1 Volumes of all the streams were 1000 ml.

2 The composition of feed solution was always kept fixed at 5% (0.1462 mol/l, around 5 brix) Sucrose and 0.025 mol/l of calcium chloride but catholyte and anolyte solutions were varied.

3 The flow rates of feed, catholyte and anolyte were 138 ml/min, 810 ml/min and 710 ml/min respectively.

4 The applied voltage (V) was varied in different runs.

5 All concentrations are expressed in mol/l.

Feed: Synthetic solutions of 5% sucrose and Calcium chloride ($CaCl_2$) were prepared with distilled water (conductivity 50-80 μMhos). Concentration of sucrose was always kept constant and concentration of $CaCl_2$ was varied.

$CaCl_2.2H_2O$: Analytical grade extra pure (99.0%), obtained from LOBA Chemie, India.

Sucrose: Analytical grade (99.95%), obtained from BDH, India.

Catholyte: During parametric studies, a dilute solution of Ethylene diamine tetraacetic acid disodium salt (EDTA) and acetic acid was used.

EDTA:	General purpose reagent (98.0%), obtained from BDH, India.
Acetic acid (AA):	Laboratory reagent (99.5%), obtained from Ranbaxy Laboratories Limited, India.
Anolyte:	A dilute solution of hydrochloric acid approximately of 0.1(M) was used and it was always kept unchanged.
HCl (Hydro Chloric acid):	Analytical grade (minimum assay 35.4%), obtained from BDH, India.

3.4 Measurement of Concentrations of the Feed Solution

Concentrations of the feed solution consisting of sucrose and $CaCl_2$, was measured through its conductivity. A calibration curve was drawn as shown in Fig A.1 (appendix A) using 5% sucrose and varying the concentrations of $CaCl_2$. This was used to determine the actual concentration from the conductivity data.

3.5 Experimental Device

The experimental setup is shown in Fig. 3.1. The electric field was applied across the cell stack by a built-in D.C. source. Voltage between the two electrodes was measured by a built-in digital voltmeter and current by a built-in digital ammeter. ED cell consists of three compartments as shown in Fig 3.1. Inside each compartment, a spacer is placed (Fig. 3.2). The CEM separates cathode compartment, and AEM separates anode compartment from the feed chamber. 1000 ml of the feed, catholyte and anolyte solutions respectively, are fed in three chambers each of which is connected to the respective compartments of the ED cell. Solutions are circulated at a constant rate by three centrifugal pumps and the solution flow rates are measured by rotameters connected to the outlets of each stream.

In the apparatus the voltage (V) was kept fixed, variation of current (I, through the membrane stack) and conductivities (λ) of the feed solution were measured with time (t). Feed stream conductivity was measured in order to analyze its Ca^{2+} ions concentration nitially and after every half an hour interval.

3.6 Experimental Procedure

Proper washing of the chambers of the ED cell and membranes was carried out before assembling the cell. Further, to avoid air bubbles in all the streams, priming was carried out. In the preliminary runs, the feed solution containing 5% sucrose and 0.025 mol/l $CaCl_2$, was circulated at a constant rate (130 ml/min) through the feed compartment. The catholyte and anolyte compositions and voltage were varied in different experimental runs. Various compositions of catholyte and anolyte streams used were:

a Both catholyte and anolyte consisting of distilled water (W).

b Catholyte containing a base (NaOH) and anolyte containing acid (HCl) of varying concentration.

c Catholyte containing different ratios of EDTA and Acetic acid (AA) with a fixed acid concentration in the anolyte.

The effects of co-current and counter current flows were also studied in these runs.

During parametric study (run no.14 to 22c), the catholyte compartment was filled with a dilute solution of EDTA and acetic acid and the anolyte compartment contained a dilute HCl solution. In the feed, the concentration of calcium ions were varied from 0.025-0.075 mol/l. Concentration of EDTA and acetic acid, flow rates of feed (80–180 ml/min), and catholyle-anolyte streams (200-830 ml/min) were varied. A constant voltage was applied in each run. The voltage was varied from 4–12 volts to study its effect on the removal.

The independent variables, current and concentrations were recorded with time. All the combinations of the runs taken for both preliminary and parametric studies are given in Appendix B (each run has been designated by a number) and the results are tabulated in Appendix C.

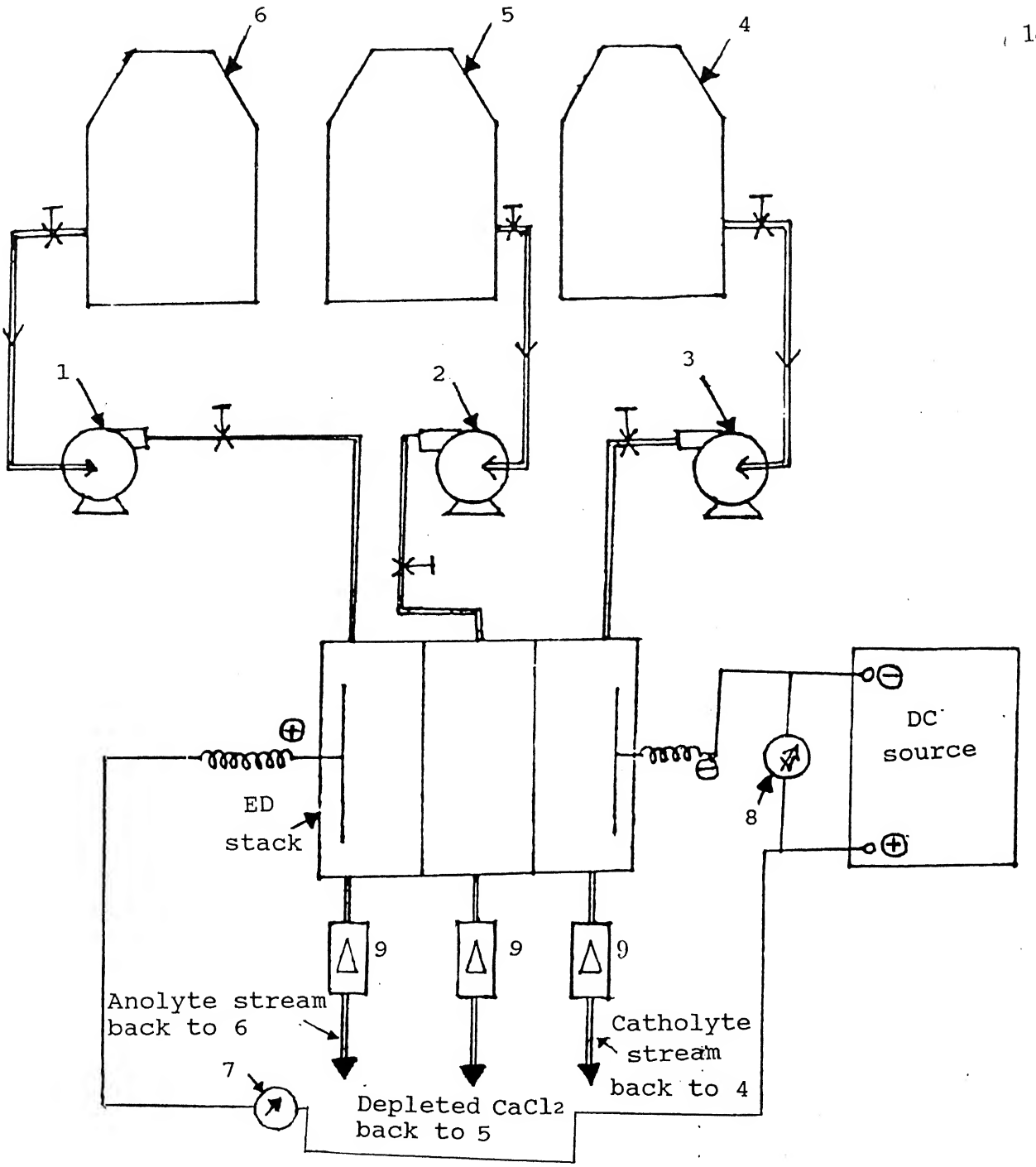


Fig. 3.1 Process flow sheet for continuous electrodialysis set up

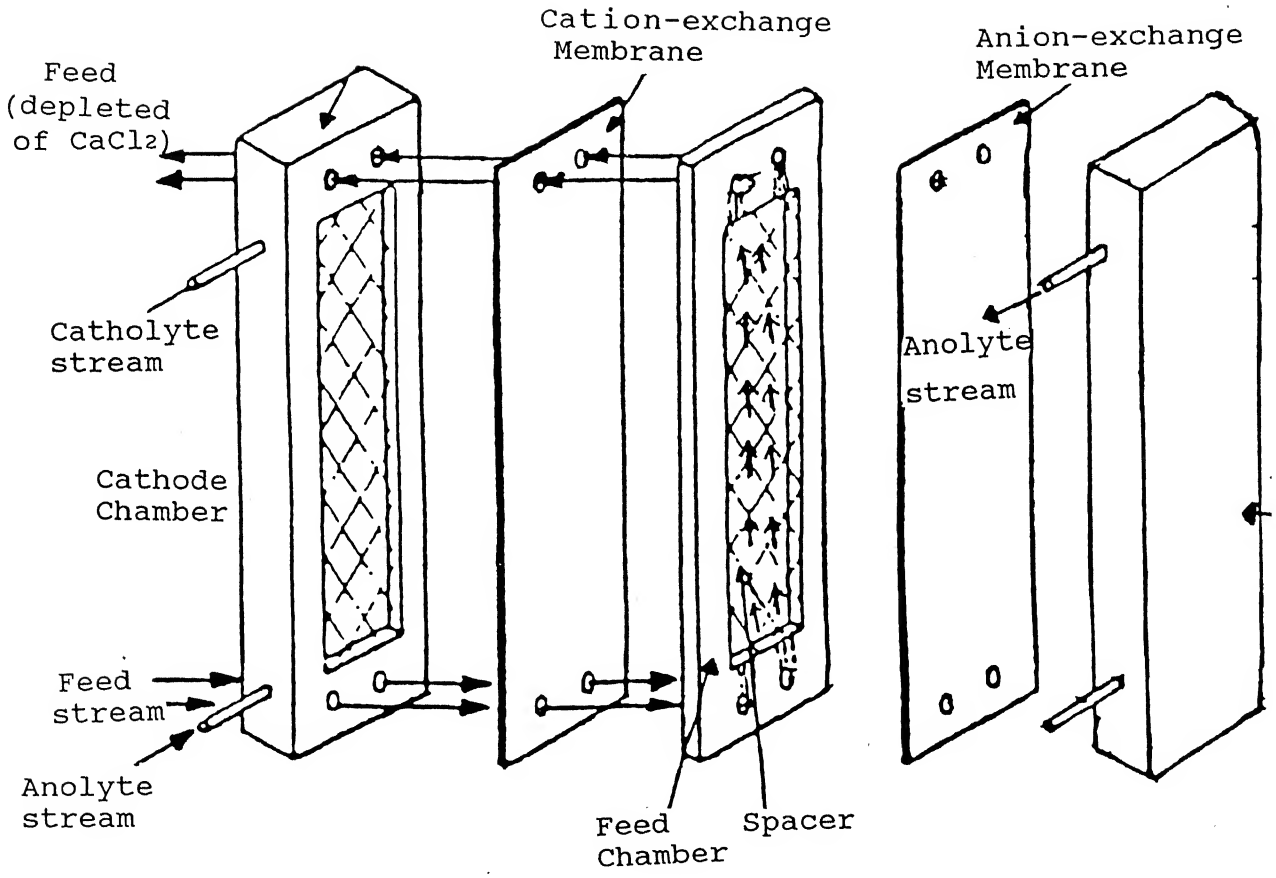


Fig. 3.2 Electrodialysis assembly

Chapter 4

Results and Discussions

4.1 Design of Experiments

4.1.1 Selection of Thin Sugar Juice

Thin sugar juice is a highly complicated mixture of various organic and inorganic compounds as shown in Table 1.1. For better analysis of results, a synthetic aqueous solution of sucrose and $CaCl_2$ was chosen for these experimental investigations. Calcium ion concentration was varied from 0.025–0.075 mol/l to study its effect on the percent removal (R). A 5% sucrose solution was selected mainly for convenient handling in laboratory scale experiments. Further, as sucrose is a non-ionic solute, its concentration may not significantly alter the percentage removal of calcium ion [2]. Also, higher concentration of sucrose increases the viscosity of the feed solution, which may cause experimental problems.

4.1.2 Observations with Preliminary Experiments

An experimental run A1 was carried out taking both catholyte and anolyte streams as distilled water under a potential difference of 2.0 Volts and 1.0 g/l. of $CaCl_2$ in 5% sucrose as feed solution. The observations indicate that probably the applied voltage was too low to carry out any removal of calcium ions in 30 mins. Then the voltage was increased to 4.0 V, A2 under the same previous conditions. The current (ammeter reading) and the Ca^{2+} ion removal started increasing with time for initial 80 mins. Then the current increment rate as well as the percentage removal rate of calcium fell and after 140 mins., the current started decreasing. The initial increment of current was probably due to a decrease in the catholyte-anolyte streams resistance for the transfer of ions (calcium and chloride respectively) from the feed solution. The decrease in current may be due to membrane fouling. Further it was noticed that the removal rate attained a maximum when the

solution current was also maximum. With a view to enhance the solution current capacity, the catholyte and anolyte streams were made more conducting by using 0.02 M NaOH and HCl solutions, instead of distilled water, respectively. The objective was that calcium ions will form calcium hydroxide in alkaline medium and will get precipitated while chloride ions will form $Cl_2(g)$ in acid medium.

The next run A3 was carried out with NaOH (0.02 M) solution as catholyte and HCl (0.02 M) solution as anolyte streams. This indicated a fall in current with time. This may be due to either neutralization of calcium ion as $Ca(OH)_2$ in the catholyte chamber followed by deposition and blocking of the membrane pores or due to an increase in the feed solution resistance for depletion of $CaCl_2$. Another interesting point to note was that the time taken for 13.8% removal (119 mins.) was half the time (60 mins.) needed in run A2. The catholyte side of CEM was found to get tremendously fouled with a white deposition and it was totally removed by dilute (0.1 M) HCl wash and some bubbles were noticed during washing, which may be due to CO_2, from which it was inferred that carbonates of calcium were formed on the membrane surface.

Increasing the anolyte and catholyte concentrations to 0.1M of NaOH and HCl, respectively, run no. 1 was carried out and the results are shown in Figs. 4.1 and 4.2. It is observed from these figures that as time progressed, the conductivity as well as current decreased. The current dropped sharply from the initial value and reached an asymptotic value within a short time. This is obvious because Ca^{2+} ion is continuously removed from the feed solution during operation, thereby decreasing the feed concentration and consequently increasing the feed solution resistance. The experimental run was stopped after the current attained an asymptotic value, the membranes were washed with 0.1 M HCl and the experiment was resumed again. Each membrane regeneration step is shown in Fig. 4.2 by a peak in the current profile. The points of membrane cleaning are further highlighted in the Fig. 4.1 by the vertical dashed lines. Upon washing with dilute HCl and restarting, appreciable enhancement of solution current was observed (Fig.4.2). After each wash the current again dropped sharply in the next operation. This is due to the deposition of Calcium carbonate on the membrane surface. Such phenomena occurred

after almost every 30-60 minutes of operation and washings were given at each vertical line stage. In 665 minutes of total run (no. 1) 91.35% of calcium ion was removed.

It was thought to use some complexing reagent in the catholyte stream to avoid the deposition of foulant layer on CEM surface. Hence a dilute solution of EDTA equimolar to that of calcium was used as the catholyte stream and distilled water was used as anolyte in run no. 2a, as shown in Fig. 4.3. It was observed that initially current increased with time and then decreased. This may be due to the fact that, as feed $CaCl_2$ concentration decreased with time, the resistance of feed chamber increased and consequently the resistances of anolyte and catholyte streams decreased. Decrease of resistance is due to its ionic permeation in these chambers; further, during this period deposition of calcium compound on the CEM surface may be less, therefore, current initially increased. It was thought that the amount of EDTA was not adequate, hence, its concentration was doubled in run no. 2b. This run, however, was for a short period, and showed a higher percent removal (Fig. 4.4). At this stage it was thought to observe the use of acidic anolyte stream on percent removal (run no. 3, Fig. 4.4) and fouling. It showed that with time, percent removal increased. Moreover there was no deposition of calcium compounds on CEM surface. Hence, next run (no. 4) was taken using lower concentration of EDTA in catholyte (equimolar to that of calcium) along with acidic anolyte stream (Fig. 4.4). It showed a lower rate of percent removal along with some deposition.

4.1.3 Use of Alkaline Catholyte Stream

Three runs were taken (Fig. 4.5) of pH levels of 6.53 (run no. 5), 9.81 (run no. 6) and 12.18 (run no. 7). It was observed that in the presence of alkali (pH=9.81) the percent removal increased, however, at high alkalinity (pH=12.18) the removal was correspondingly low. In all the three runs in presence of EDTA fouling was severe. Hence the use of alkaline medium in catholyte was found not attractive.

4.1.4 Use of Acetic Acid in Catholyte Stream

Fig. 4.6 (run nos. 8 and 9) it is clear that acetic acid in presence of EDTA gives r results than with simple acetic acid in catholyte stream. Further, no fouling was ved.

4.1.5 Observation with Higher Voltage

3 volt ED operation was carried out (Fig. 4.7) in run nos. 10, 11 and 12. Compared to ier data reported with 4 volts, an increase in applied voltage increased calcium removal. omparison of Fig. 4.7 with Fig. 4.6 at time 240 minutes shows that percent removal eased to about almost 16-20% in each case. Therefore applied voltage was observed to an important parameter to study.

4.1.6 Use of Counter-Current Flow

l the runs, as earlier discussed (*i.e.*, upto run number 12), were carried out where the ed flow direction was co-current to anolyte and catholyte. It was thought to use counter-urrent flow. The effect of these two types of flow counter-current (run 13) and co-current un 12), on percent removal are compared in Fig. 4.8. Counter-current flow was clearly ound better than co-current flow, in terms of percent removal, because in the former case lways a higher concentration gradient is maintained. So in all the subsequent runs the ollowing combination was chosen for systematic parametric analysis.

Catholyte: EDTA and Acetic acid solution.

Anolyte: Dilute solution of HCl (0.1 M).

Flow: Feed solution counter-current with the catholyte and anolyte stream.

Parameters varied were:

1 Feed (80,130 and 180 ml/min.)

2 Catholyte and anolyte flow (200, 400 and 830 ml/min.)

3 Feed calcium ion concentration (0.025, 0.05 and 0.075 mol/l).

4 EDTA concentration in catholyte stream (0.00625, 0.0125, 0.025, 0.0375, 0.05, 0.075 mol/l).

5 Acetic acid concentration in catholyte stream (0.0, 0.025, 0.05, 0.075, 0.10 and 0.15 mol/l).

6 Voltage (4, 8 and 12).

4.2 Limiting Current Density

It is necessary for any design analysis of ED that all the investigations are carried out below limiting current density. Hence, a plot of V/I *vs.* $1/I$ was obtained as shown in Fig.4.9. The absence of any bend in the curve indicates that all the experimental runs were taken below limiting current density condition [11]

4.3 Analysis of the Parameters

4.3.1 Effect of EDTA (disodium salt) Concentration

EDTA is primarily responsible for the removal of Ca^{2+} ion by complexation. Its solution is acidic in nature. On increasing the amount of EDTA, the percent removal increased as is evident in Figs. 4.10 and 4.11 for two different acetic acid concentrations of 0.025 and 0.1 mol/l in catholyte and for a particular concentration (0.025mol/l) of calcium in the feed solution. This may be explained as the lower doses of EDTA is consumed much faster with incoming calcium ions. Thus after sometime the catholyte solution pH is increased and hence the alkaline catholyte stream causes fouling on the membrane surface. Whereas, with higher dosage of EDTA, the catholyte pH is never allowed to be alkaline, so no deposition occurs and higher percent removal was obtained.

4.3.2 Effect of Concentration of Acetic Acid

Without acetic acid, the percent removal was found to be low compared to higher concentration of acetic acid as shown in Fig. 4.12 and 4.13. However much higher dosages of acetic acid did not show significant enhancement of percent removal. This may be due to the fact that a small amount of acetic acid (equimolar to that of calcium ion) was just

sufficient to maintain the solution pH acidic and thus preventing the deposition of calcium on the membrane surface. Studies with the variation of concentrations of acetic acid and EDTA show that the former mainly helps in maintaining acidic medium of catholyte stream, while the latter also plays a role in complexing with Ca^{2+} ions to prevent fouling of membrane. Merely increasing the EDTA concentration without adding acetic acid also maintains the desired acidity of the catholyte. However, EDTA being costlier than acetic acid, the latter is added. Whereby, the acidity can be maintained by reducing the amount of EDTA used. (Fig. 4.6 also depicts the same).

4.3.3 Effect of Concentration of Calcium Ion

Figs. 4.14 and 4.15 show the percent removal as function of operating time for different $CaCl_2$ concentrations (0.025, 0.05 and 0.075 mol/l) in the feed. The experimental data reported in both the Figs. 4.14 and 4.15 correspond to:

$$C_{AA} = 2 \times C_{Ca};\ C_{EDTA} = C_{Ca}$$

i.e., only the calcium concentrations are different. Both the figures show similar trends *i.e.* a percent removal of around 70–80% after 240 mins. of operation. It is also seen that an increase in feed Ca^{2+} ion concentration lowers the percent removal. The reason may be due to that at higher $CaCl_2$ concentration the ionic strength of the solution is more which causes more polarization. Thus the movement of the ions is slowed down. Plotting the percent removal at a particular time (200 min.) against the concentration of calcium it is clearly evident from Fig. 4.16 that at lower Ca^{2+} concentration percent removal is more and it decreased with increase of concentration. Further, from the concept of Donnan potential [22]

$$\bar{C}_+ = \frac{\gamma_+\gamma_-}{\bar{\gamma}_+\bar{\gamma}_-} \times \frac{C_+^2}{\bar{C}_-} \tag{4.1}$$

Eqn. 4.1 shows that the flux of co-ions through an ion-exchange membrane may be reduced to low values. In addition, it indicates that as the fixed ion concentration in the membrane increases, co-ion flux decreases. Therefore, ED operation is advantageous with dilute solutions and is generally carried out in the range of 0.001 to 0.1 molality.

4.3.4 Effect of Voltage

The voltage effects were studied with three different feed Ca^{2+} concentrations of 0.025, 0.05 and 0.075 mol/l and are shown in Figs. 4.17, 4.18 and 4.19, respectively. It is evident from these plots of percent removal against time, that at 8 volts, there is a significant increase in the rate of calcium removal compared to 4 volts. However, any further rise in voltage resulted in a marginal increase of the percent removal. This was observed irrespective of calcium ion concentrations. The non proportionate increase of percent removal beyond 8 volts may be due to the fact that at a very high voltage, most of the extra driving force was consumed in carrying out solvent (Electro-Osmosis). Considering energy analysis, the optimum voltage should be determined for a particular concentration of feed solution. Further, it was noted that at lower voltages (4 V) the percent removal showed a more or less linear increase with time for the duration of the experiments.

4.3.5 Effect of Feed Flow Rate

The feed flow rate variation was studied and the observed results are shown in Fig. 4.20. This indicates that on increasing feed flow rate from 80 to 130 ml/min the percent removal increased. This is due to the increased turbulence which decreases the diffusional resistance at the feed side film, thereby increasing the mass transfer. However, on further increment to 180 ml/min the change in percent removal is insignificant.

4.3.6 Effect of Catholyte and Anolyte Flow Rate

The catholyte and anolyte flow rate variation were studied with respect to percent removal. Experiments were carried out keeping the flow rates same for both catholyte and anolyte. Fig. 4.21 shows that at higher flow rate, the percent removal was higher. At lower flow rate some serious problems were observed *ie,*

1 Production of enormous amount of $H_2(g)$ and $Cl_2(g)$ gases.

2 Tripping of the anolyte and catholyte pumps and several operational problems.

Cathode: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$2H^+ + 2e \rightleftharpoons H_2(g)$

$Ca^{2+} + 2H_2O \rightleftharpoons Ca(OH)_2 + 2H^+$

Anode: $2Cl^- \rightleftharpoons Cl_2(g) + 2e$

These gases caused an obstruction to the catholyte and anolyte streams which tripped the pumps during experiment with 200 ml/min. Therefore highest flow rate obtainable with this set-up (*ie*, 830 ml/min.) was utilized to overcome the above problems associated with the low flow rates for both anolyte and catholyte. Further, higher flow rates resulted in a higher percent removal (Fig. 4.21).

4.4 Analysis of ED Operation

4.4.1 Fitting of Experimental Data

To deal with these extensive sets of experimental data, it was felt necessary to fit the data on a suitable and simple mathematical expression. The percent of calcium removed can be correlated with time using an equation of the following type,

$$R = \alpha \cdot t^{\beta} \tag{4.2}$$

Each experimental run was fitted using expression 4.2 and values of α, β are recorded in Appendix C. Correlation coefficients of 0.99 and above were found, suggesting an excellent fitting of data.

4.4.2 Correlation Between Percent Removal and its Influencing Variables

It was thought appropriate to obtain a correlation between percent removal and its influencing variables like calcium ion concentrations in fluid, concentration of EDTA and acetic acid in catholyte, applied voltage and flow rates of feed and catholyte-anolyte. Such a correlation may help to design for an efficient ED system dealing with calcium ion

separation from sugar solution. All other variables influencing percent removal were kept constant throughout.

At the microscopic level calcium ion reacts both with the acetic acid as well as with EDTA. The former forms a less stable complex with calcium. It keeps the solution pH low (*i.e.*, in the acidic range) thereby the precipitation of calcium on the membrane surface is prevented. The role of voltage is very prominent. To relate all the influencing variables to percent removal, it was thought necessary to obtain dimensionless forms of variables by expressing them as fractions of their respective maximum values. Hence the percent removal R was correlated to be a function of the following type.

$$R = K \cdot A^{x_1} B^{x_2} C^{x_3} D^{x_4} E^{x_5} \tag{4.3}$$

where

$$A = \frac{C_{\mathrm{Ca(max)}}}{C_{\mathrm{Ca}}}$$

$$B = \frac{C_{\mathrm{Ca}} + C_{\mathrm{EDTA}}}{C_{\mathrm{Ca}}}$$

$$C = \frac{C_{\mathrm{Ca}} + C_{\mathrm{AA}}}{C_{\mathrm{Ca}}}$$

$$D = \frac{V_{\mathrm{max}}}{V}$$

$$E = \frac{Q_{\mathrm{F}}}{Q_{\mathrm{CA}}}$$

and x_1, x_2, x_3, x_4, x_5, K are constants of equation (4.3).

Here, the maximum concentration of calcium and Voltage represents the maximum values taken for the entire set of experiments. When the concentration of acetic acid becomes zero *ie,* only EDTA is present in the catholyte stream, then the term B will only take into consideration the concentration effect. Here all the concentrations are the initial values taken for each run. Further, all the values of percent removal are taken at time greater than 225 mins (*i.e.*, when there is no appreciable change in percent removal). The values of R were recalled from fitted eqn. (4.2), at time 225 min.

On regression analysis with all the experimental data, the following expression is obtained

$$R = 0.625 \cdot A^{0.127} B^{0.075} C^{0.063} D^{-0.77} E^{0.143} \tag{4.4}$$

The correlation coefficient between the data sets of R obtained from eqn. (4.2) and (4.4), is 0.91. This suggests a satisfactory agreement which is also shown in Fig. 4.22. Another effort was made to check the overall effect of the concentration terms, *i.e.*, all the concentration terms when coupled and related as follows:

$$R = M \cdot (ABC)^{y_1} D^{y_2} E^{y_3} \tag{4.5}$$

where

$$ABC = \frac{C_{\mathrm{Ca}} + C_{\mathrm{EDTA}} + C_{\mathrm{AA}}}{C_{\mathrm{Ca}}}$$

and D, E are the same as earlier.

On regressing, the values of the constants are obtained as shown below

$$R = 0.617 \cdot (ABC)^{0.145} D^{-0.777} E^{0.161} \tag{4.6}$$

Correlation coefficient between the data sets, obtained from eqn. (4.2) and (4.6) is 0.88. This, however, suggests only a reasonable agreement. All the above relations are valid in the following range:

Concentration of Calcium ion	0.025	to	0.075 mol/l
Concentration of EDTA	0.00625	to	0.075 mol/l
Concentration of acetic acid	0.00	to	0.15 mol/l
Voltage or applied potential	4.0 V	to	12.0 V
Feed flow rate	80.0	to	180.0 ml/min
Catholyte and Anolyte flow rate	200.0	to	830.0 ml/min

4.4.3 Analysis of the Regression Results

It is clearly evident that the term D is the most important parameter to determine percent removal. This indicates that on increasing the voltage the percent removal also increases.

The term A represents the effect of calcium ion concentration in feed solution. If the concentration of calcium decreases, the percent removal increases, which exactly agrees with the ED phenomena. This is not so prominent as that of the voltage.

The term E represents the ratio of the feed and catholyte flow rates. The positive sign of the constant (x_5, or y_3) indicates that with an increase of the catholyte flow rate, for a given value of the feed flow rate, the percent removal increases. The probable reason was already explained in section 4.3.6.

The terms B and C represent the effects of EDTA and acetic acid, respectively. The positive sign of the value of the constants x_2 and x_3 indicates that the percent removal will increase with an increase in concentration both of EDTA and Acetic acid. But the effect is very small compared to that of voltage.

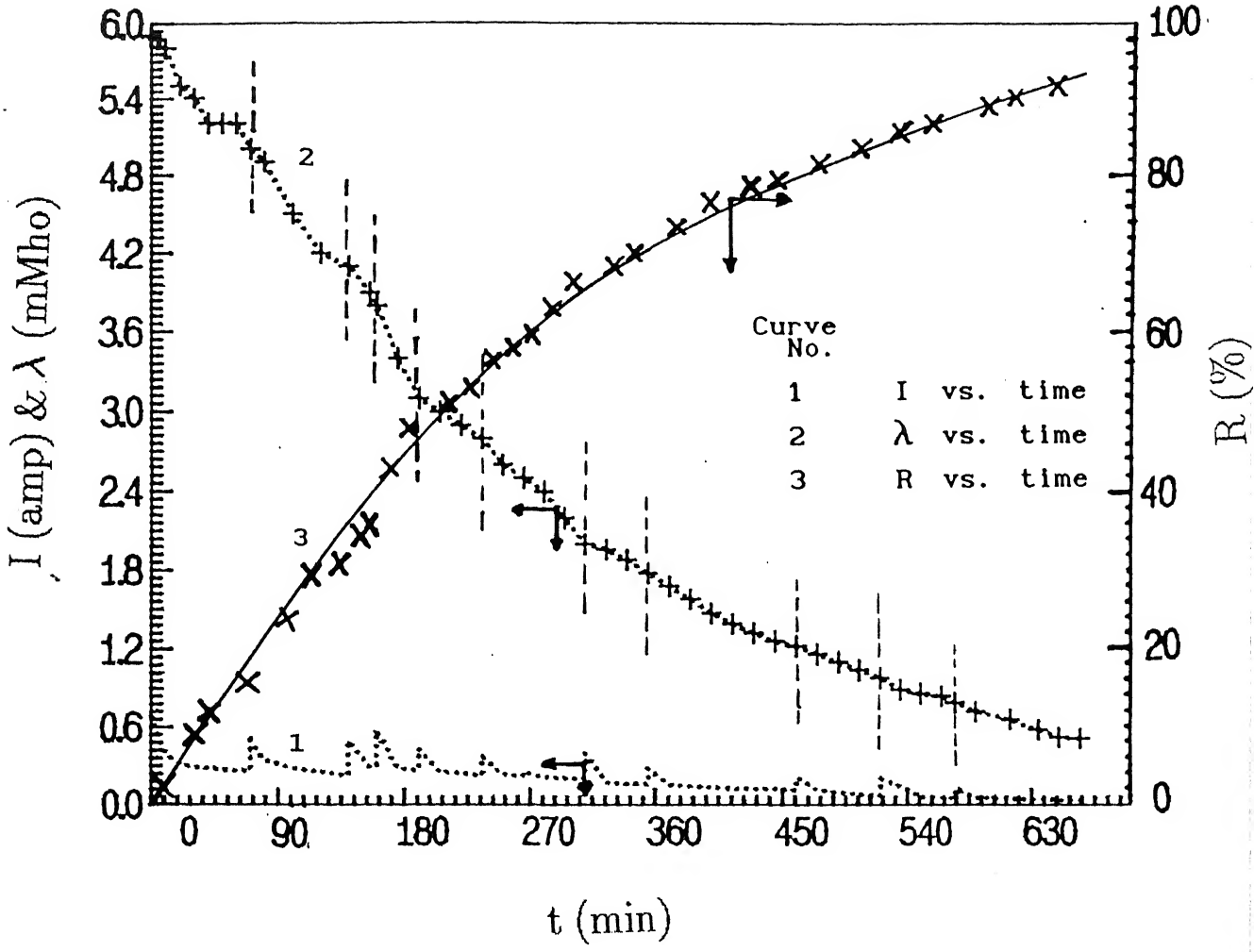


Fig. 4.1 Current,conductivity and percent removal vs time plot for run no.1

Concentration(mol/l)		Flowrate(ml/min)	
Feed(Ca^{2+})	0.025	Feed	130
Catho(NaOH)	0.1	Catholyte	810
Anolyte(HCl)	0.1	Anolyte	710

Voltage - 4 V

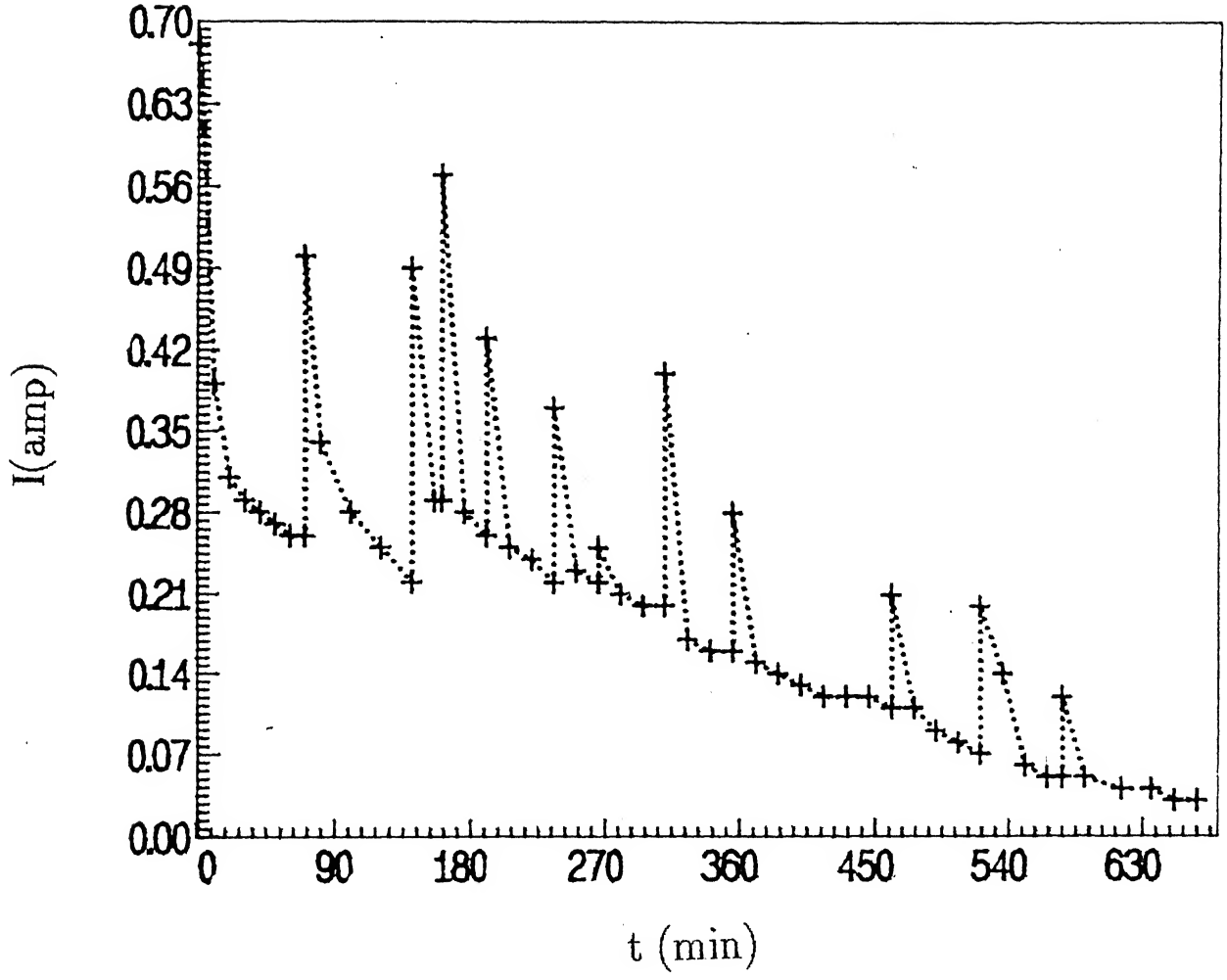
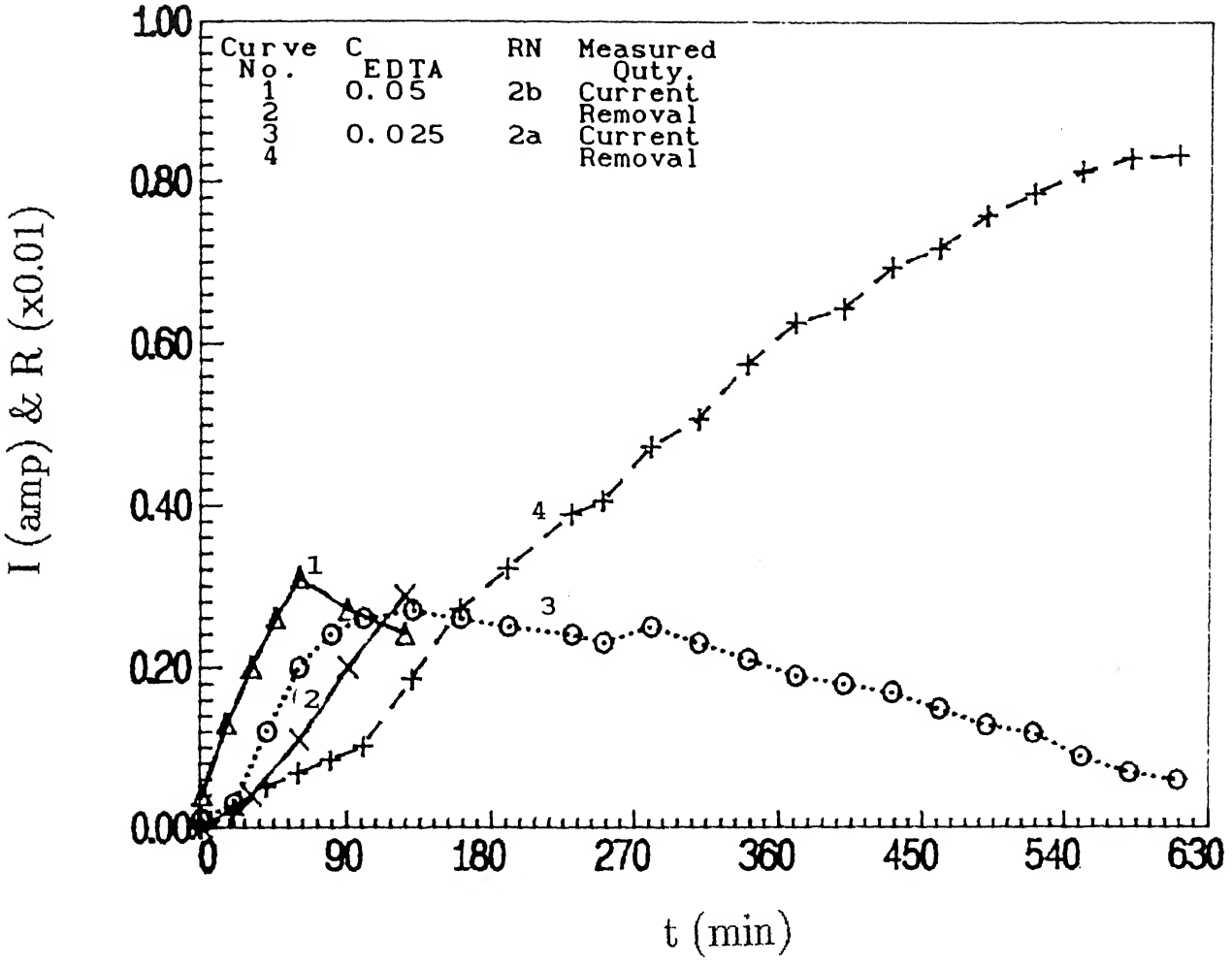


Fig. 4.2 Current vs time plot for run no.1



4.3 Current and percent removal vs time plot for run nos. 2a

Flow rates(ml/min)		Concentration(mol/l)	
Feed	130	Feed(Ca^{2+})	0.025
Catholyte	810	Anolyte	D.W.
Anolyte	710	Catholyte EDTA	varied

Voltage - 4 V

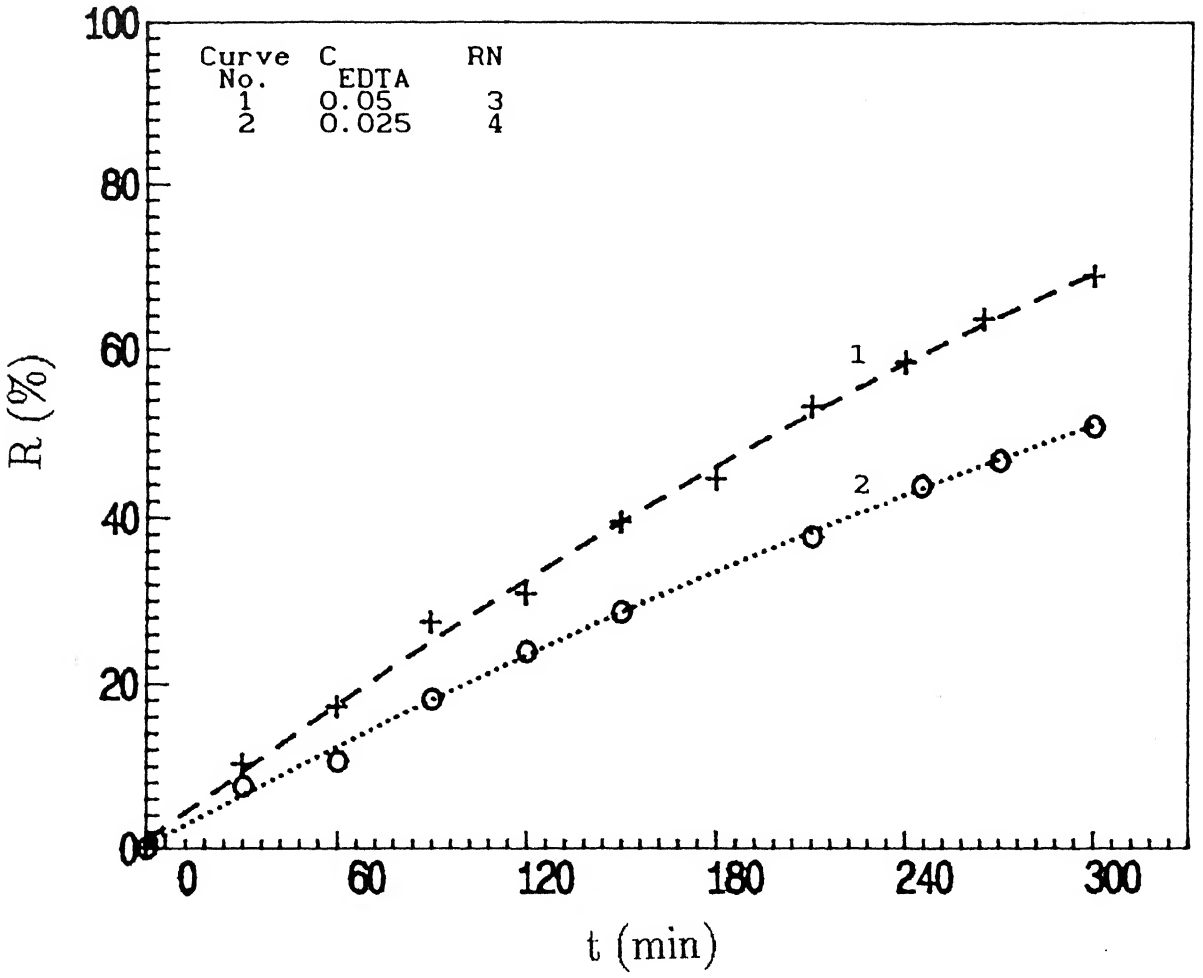


Fig. 4.4 Percent removal vs time plot for run nos. 3 & 4

Flow rates (ml/min)		Concentration(mol/l)	
Feed	130	Feed(Ca^{2+})	0.025
Catholyte	810	Anolyte(HCl)	0.1(pH = 1.19)
Anolyte	710	Catholyte EDTA	varied

Voltage - 4 V

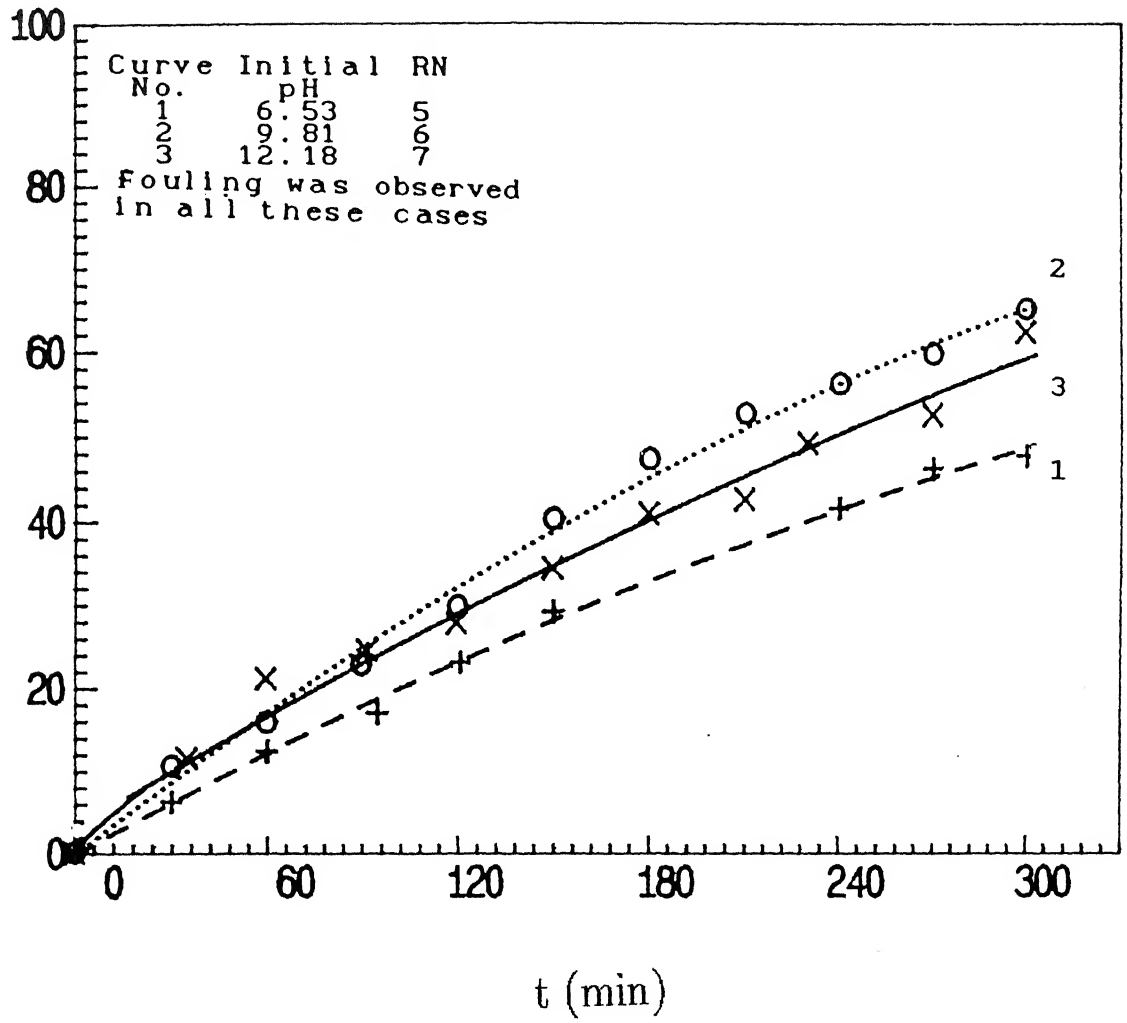


Fig. 4.5 Percent removal vs time plot for run nos. 5,6 & 7

Flow rates(ml/min)		Concentration(mol/l)	
Feed	130	Feed(Ca^{2+})	0.025
Catholyte	810	Anolyte(HCl)	0.1
Anolyte	710	Catholyte(EDTA +NaOH)	0.025

Voltage - 4 V

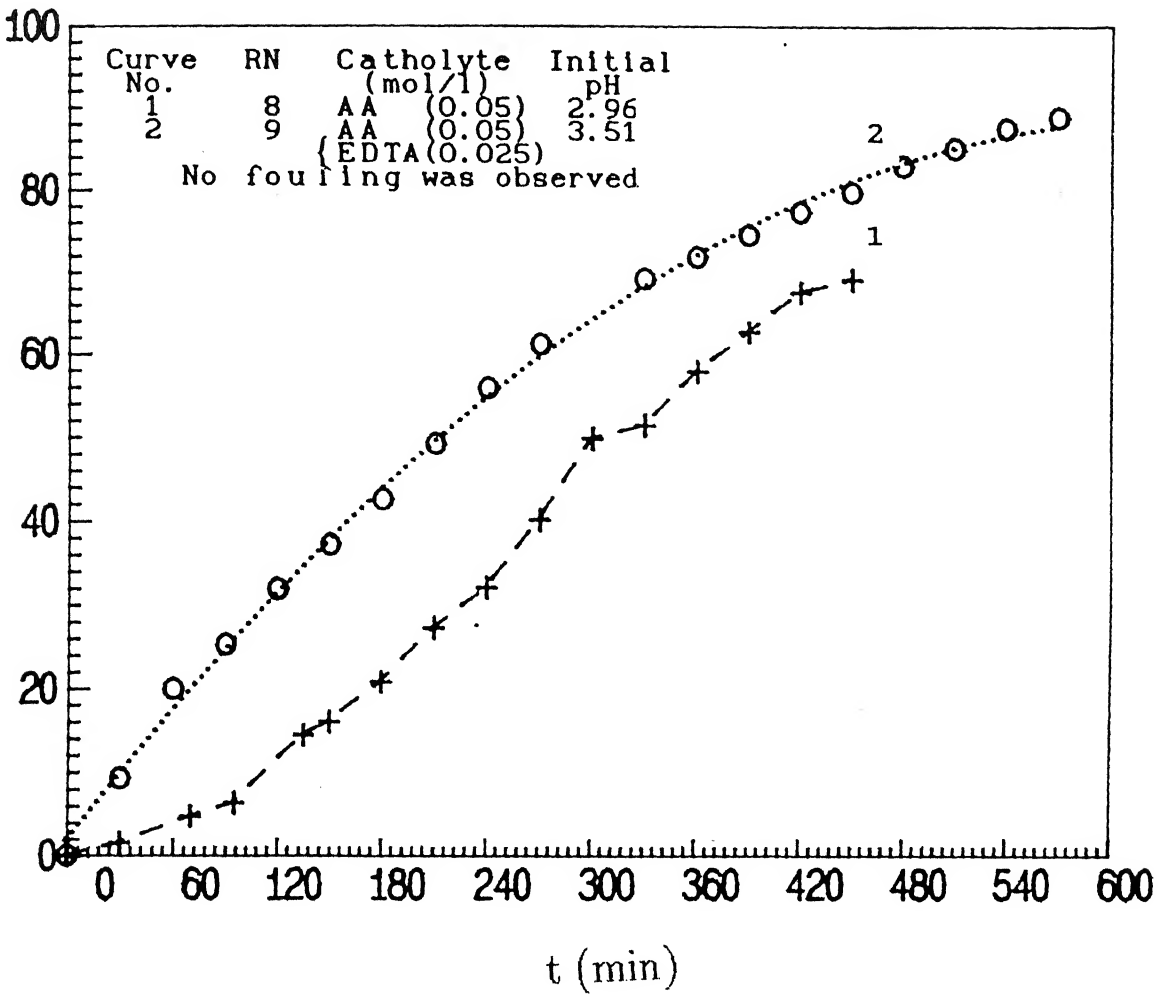


Fig. 4.6 Percent removal vs time plot for run nos. 8 & 9

Flow rates (ml/min)		Concentration(mol/l)	
Feed	130	Feed(Ca^{2+})	0.025
Catholyte	810	Anolyte(HCl)	0.1
Anolyte	710		

Voltage - 4 V

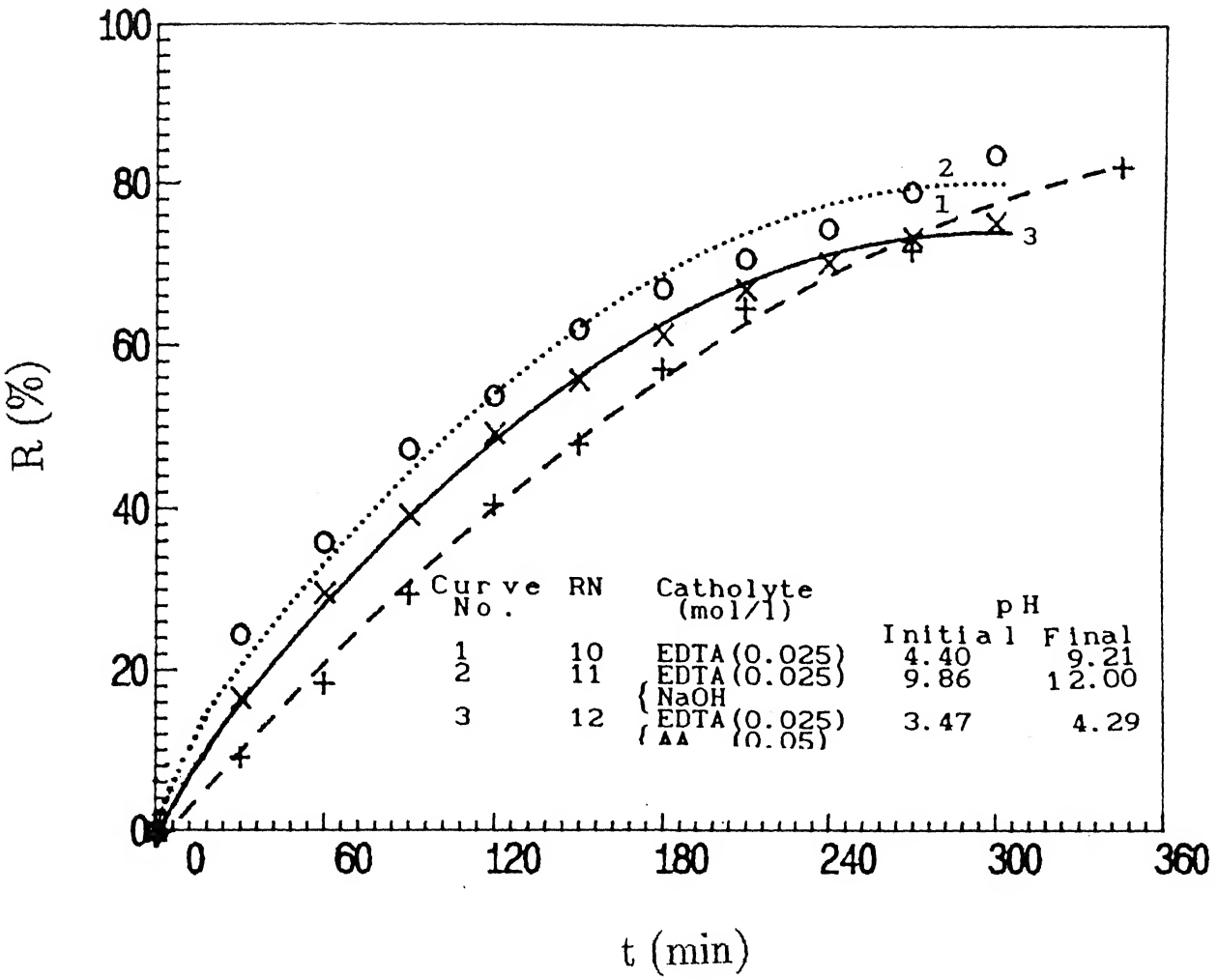


Fig. 4.7 Percent removal vs time plot for run nos. 10, 11 & 12

Flow rates (ml/min)		Concentration (mol/l)	
Feed	130	Feed (Ca^{2+})	0.025
Catholyte	810	Anolyte (HCl)	0.1
Anolyte	710		

Voltage - 8 V

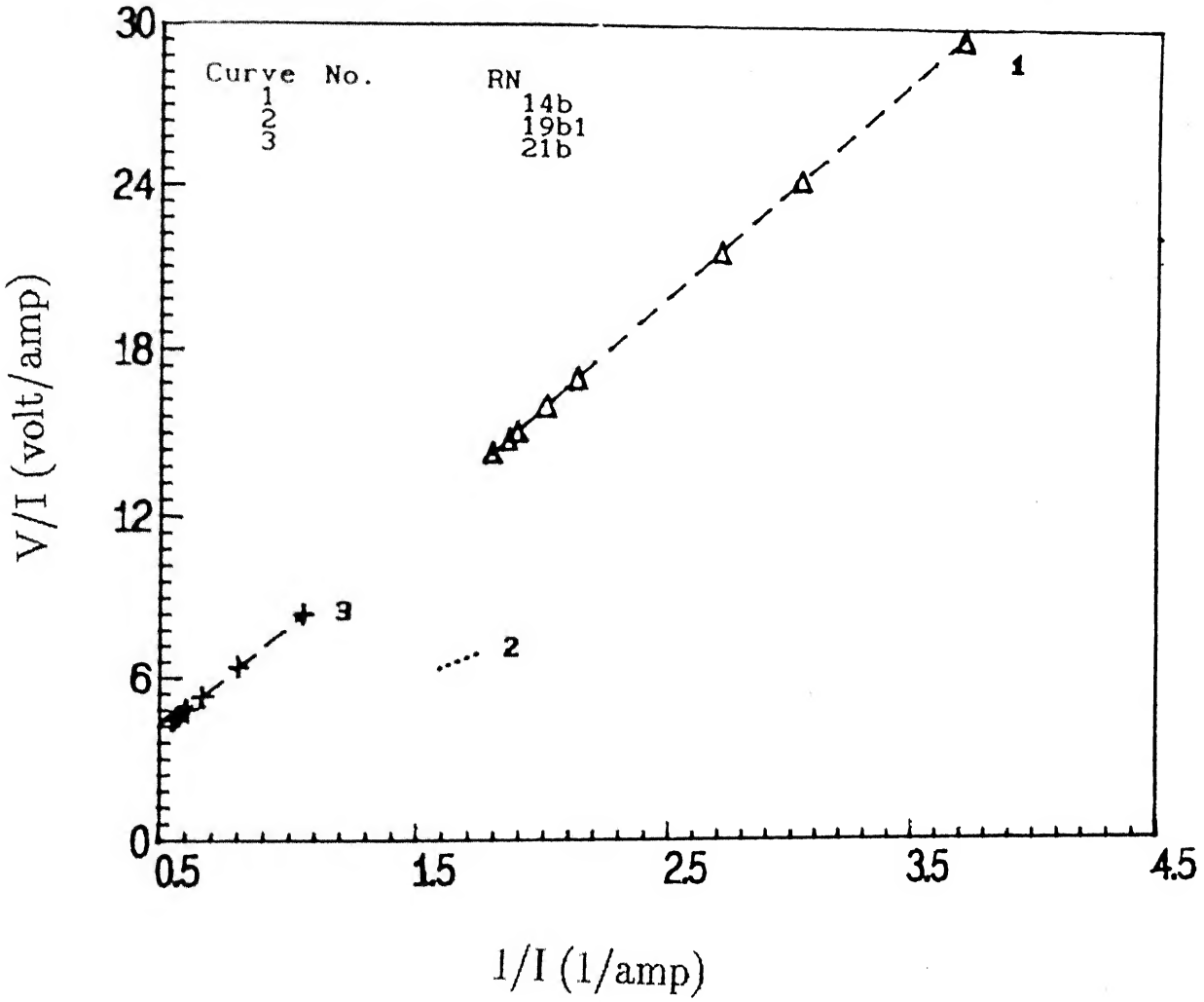


Fig. 4.9 Plot of V/I vs 1/I

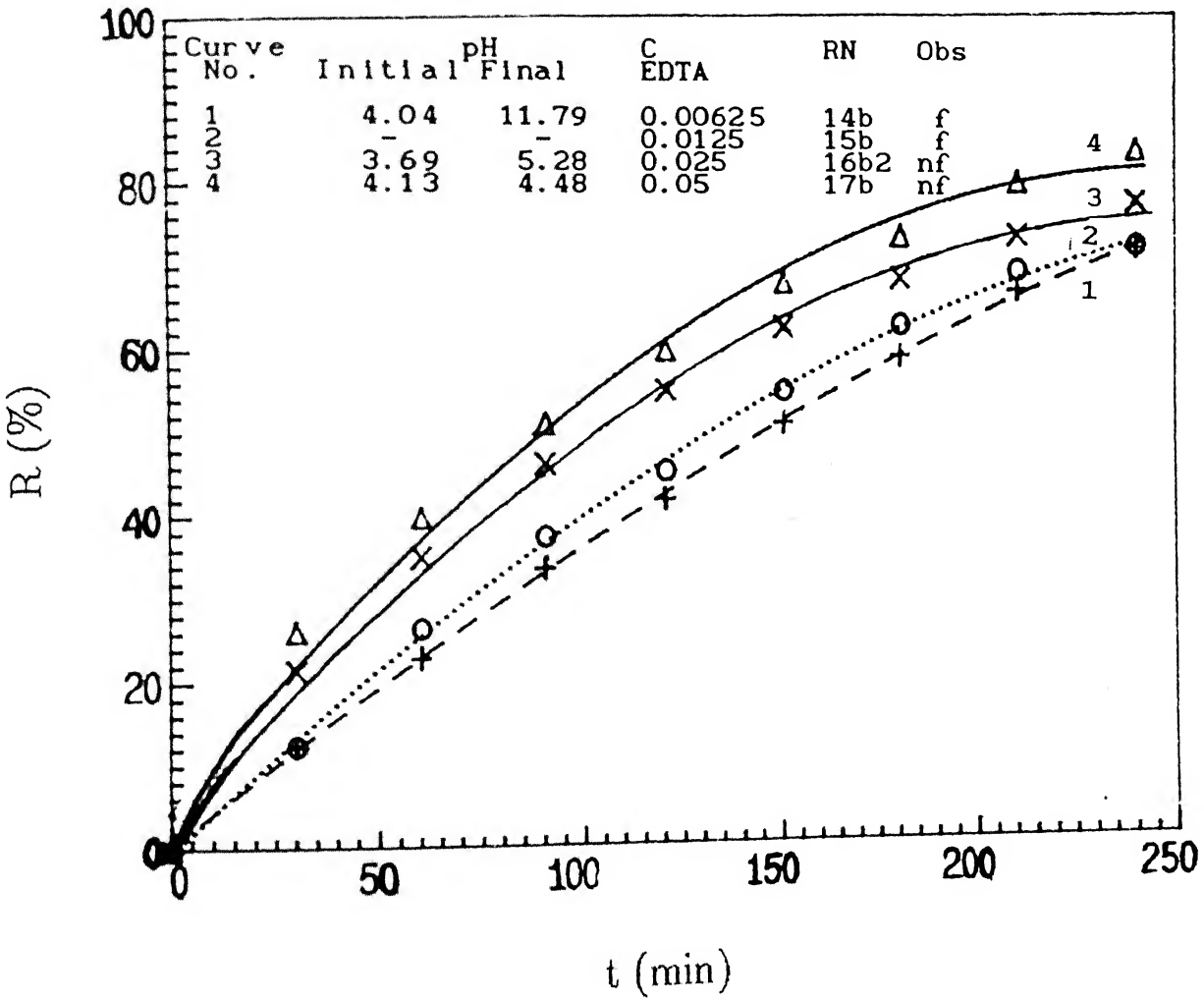


Fig. 4.10 Effect of EDTA concentration in catholyte stream on percent removal

Flow rates (ml/min)		Concentration (mol/l)	
Feed	130	Feed (Ca^{2+})	0.025
Catholyte	830	Catholyte (EDTA)	varied
Anolyte	830	Catholyte (AA)	0.025

Voltage - 8 V

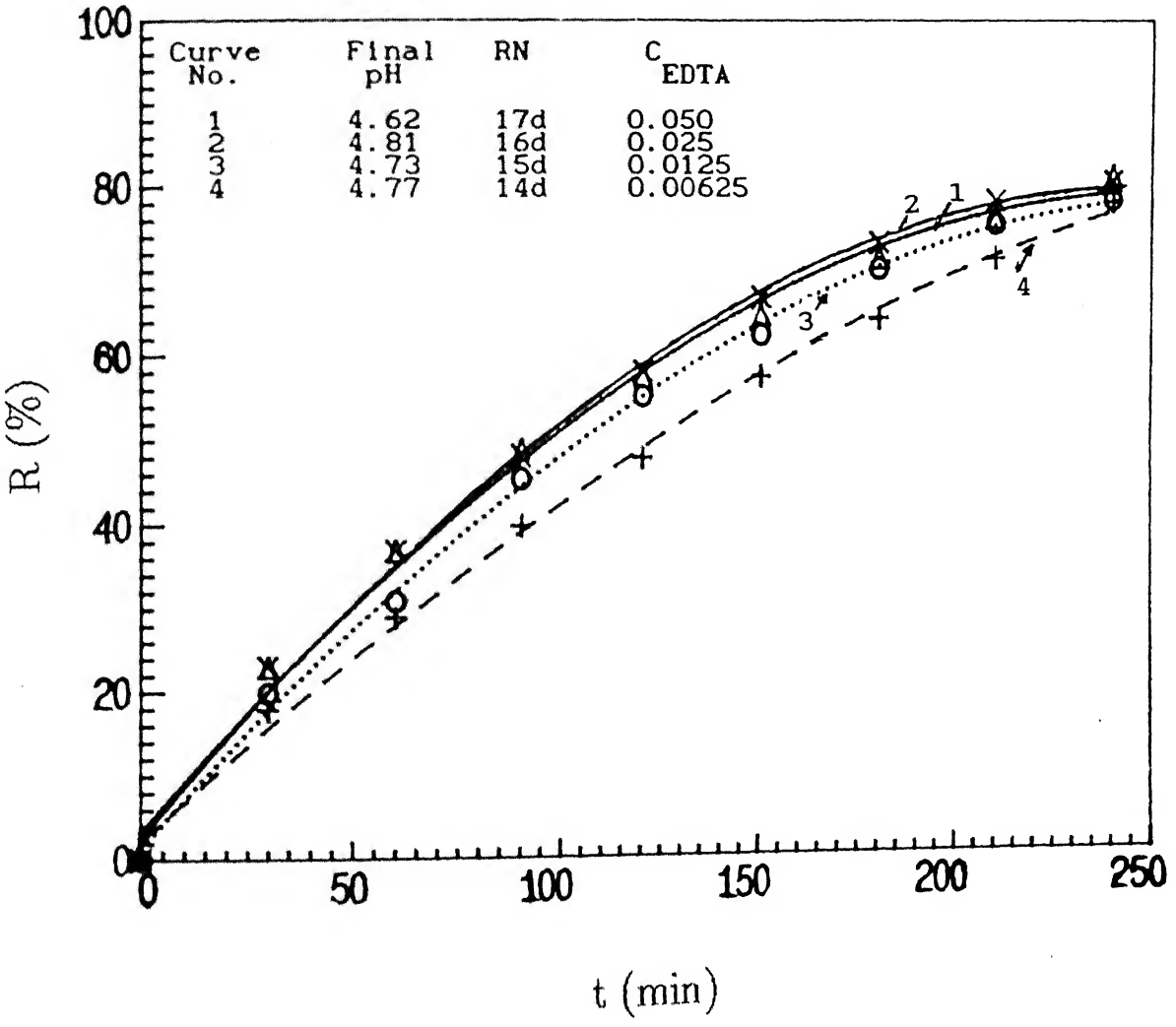


Fig. 4.11 Effect of EDTA concentration in catholyte stream on percent removal

Flow rates(ml/min)		Concentration(mol/l)	
Feed	130		
Catholyte	830	Feed(Ca^{2+})	0.025
Anolyte	830	Catho- EDTA	varied
		lyte (AA	0.1

Initial pH ~ 3.69; Voltage - 8 V

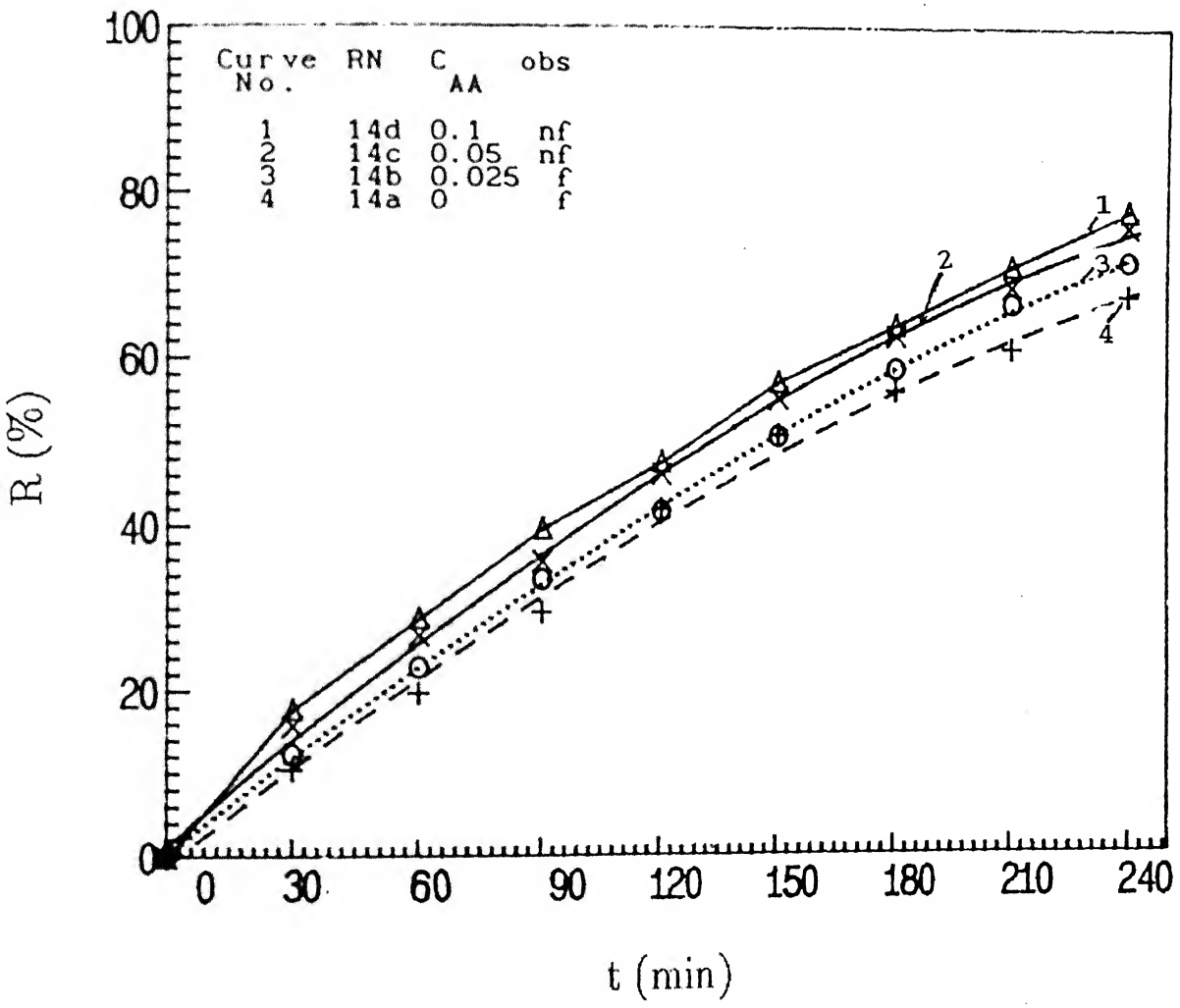


Fig. 4.12 Effect of acetic acid concentration in catholyte stream on percent removal

Flow rates (ml/min)		Concentration (mol/l)	
Feed	130		
Catholyte	830	Feed (Ca^{2+})	0.025
Anolyte	830	Catholyte EDTA	0.00625
		Catholyte AA	varied

Voltage - 8 V

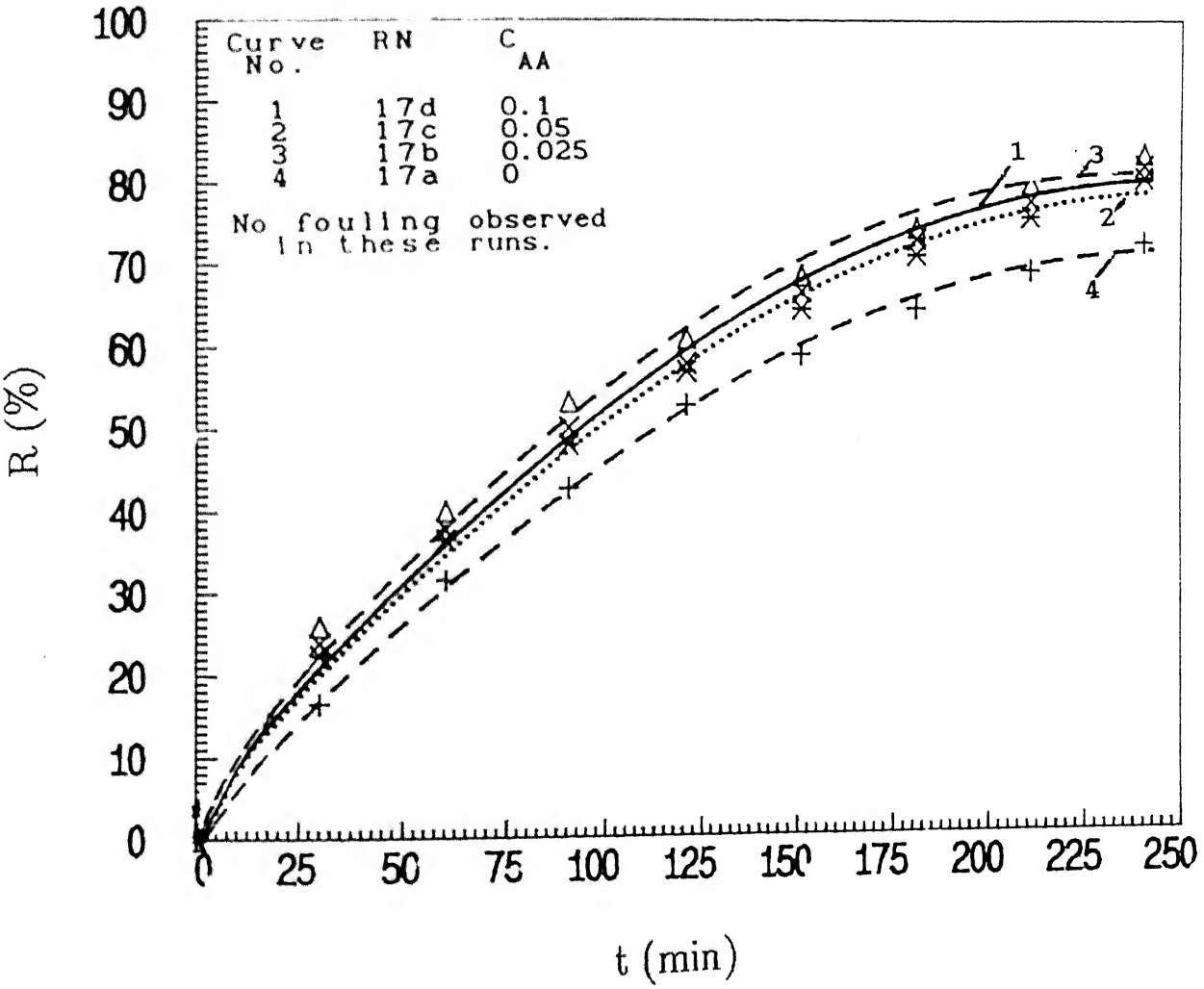


Fig. 4.13 Effect of acetic acid concentration in catholyte stream on percent removal

Flow rates (ml/min)		Concentration (mol/l)	
Feed	130		
Catholyte	830	Feed (Ca^{2+})	0.025
Anolyte	830	Catholyte EDTA	0.05
		Catholyte AA	varied

Voltage - 8 V

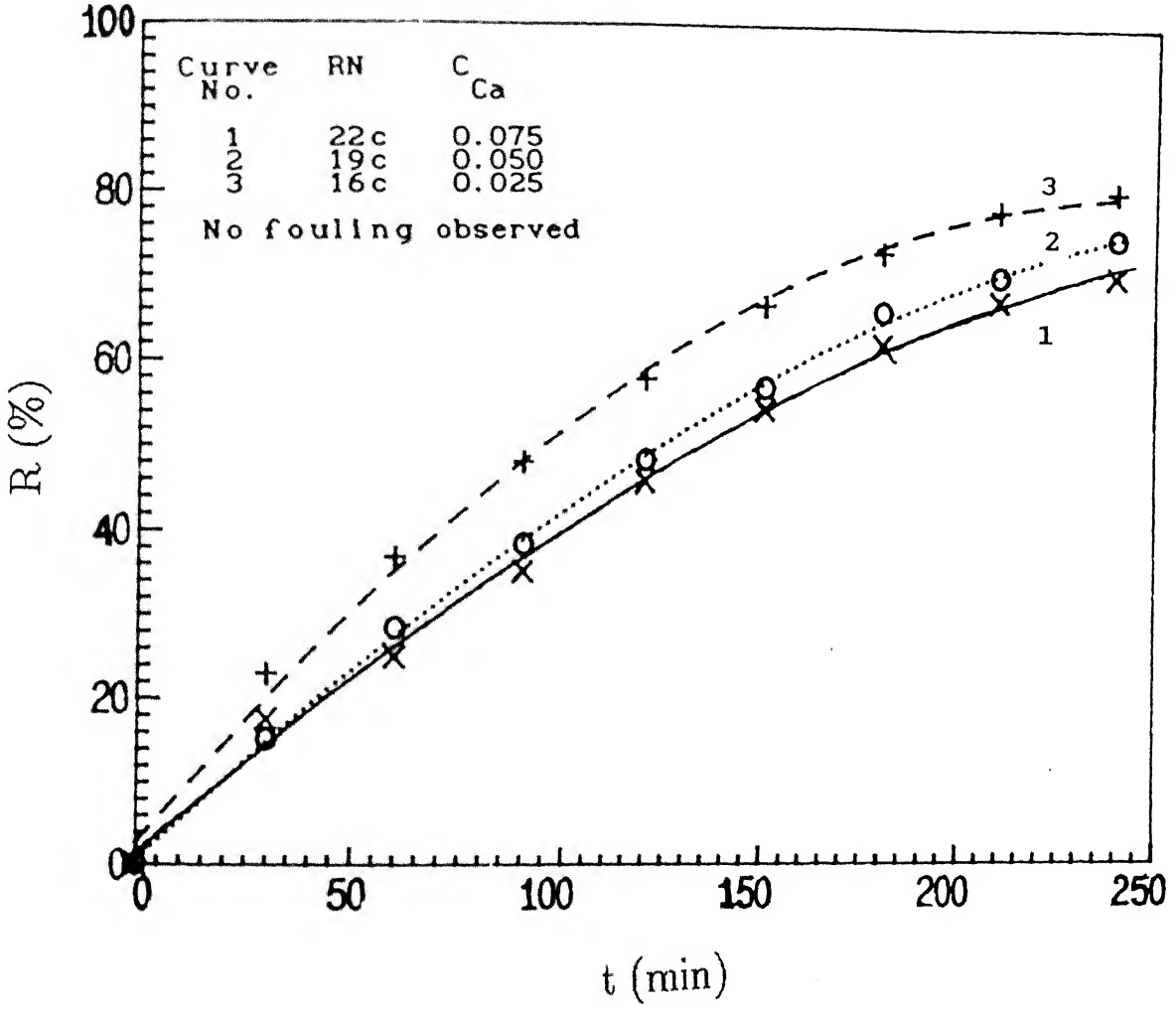


Fig. 4.14 Effect of calcium concentration in the feed stream on percent removal

Flow rates (ml/min)		Concentration (mol/l)	
Feed	130	Feed (Ca^{2+})	varied
Catholyte	830	Catholyte { EDTA	1 } x C_{Ca}
Anolyte	830	AA	2

Voltage - 8 V

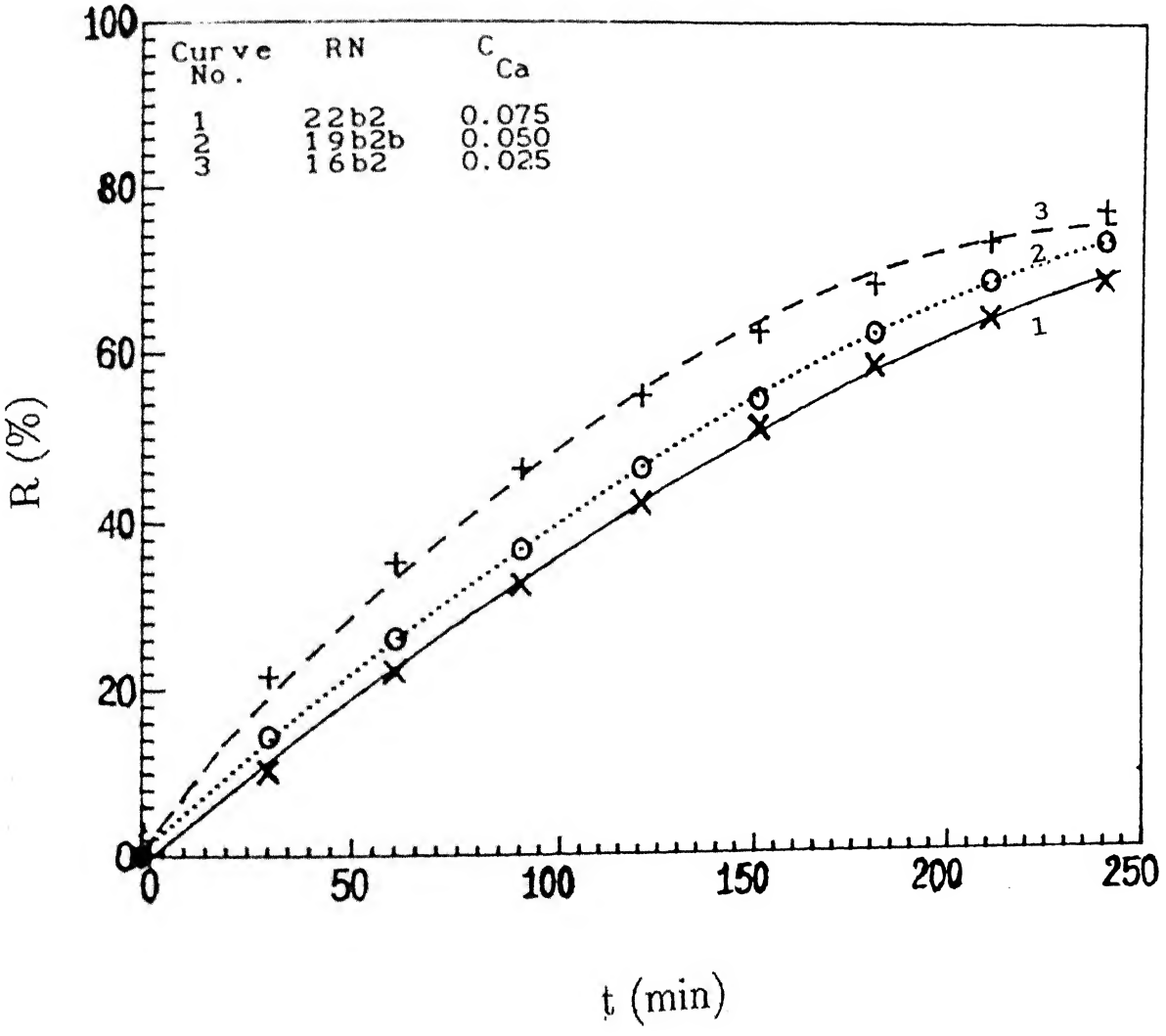


Fig. 4.15 Effect of calcium in the feed stream on percent removal

Flow rates (ml/min)		Concentration (mol/l)	
Feed	130		
Catholyte	830	Feed (Ca^{2+})	varied
Anolyte	830	Catholyte ($\frac{EDTA}{AA}$)	1 x C_{Ca}

Voltage - 8 V

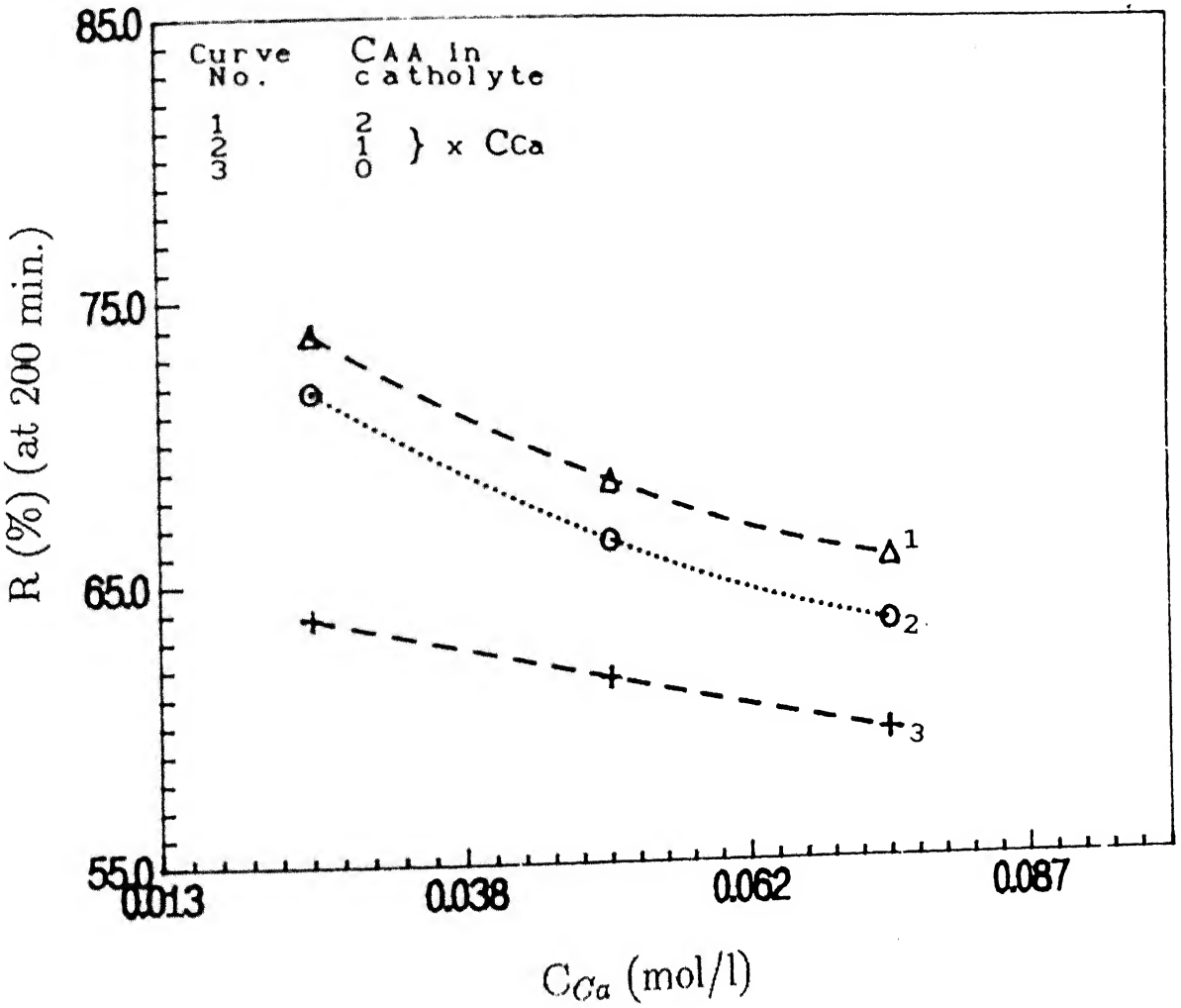


Fig. 4.16 Comparison of percent removal at 200 min. with concentraiton of calcium ion. The three curves represent different acetic acid concentration.

Flow rates(ml/min)
Feed 130
Catholyte 830
Anolyte 830

Voltage - 8 V

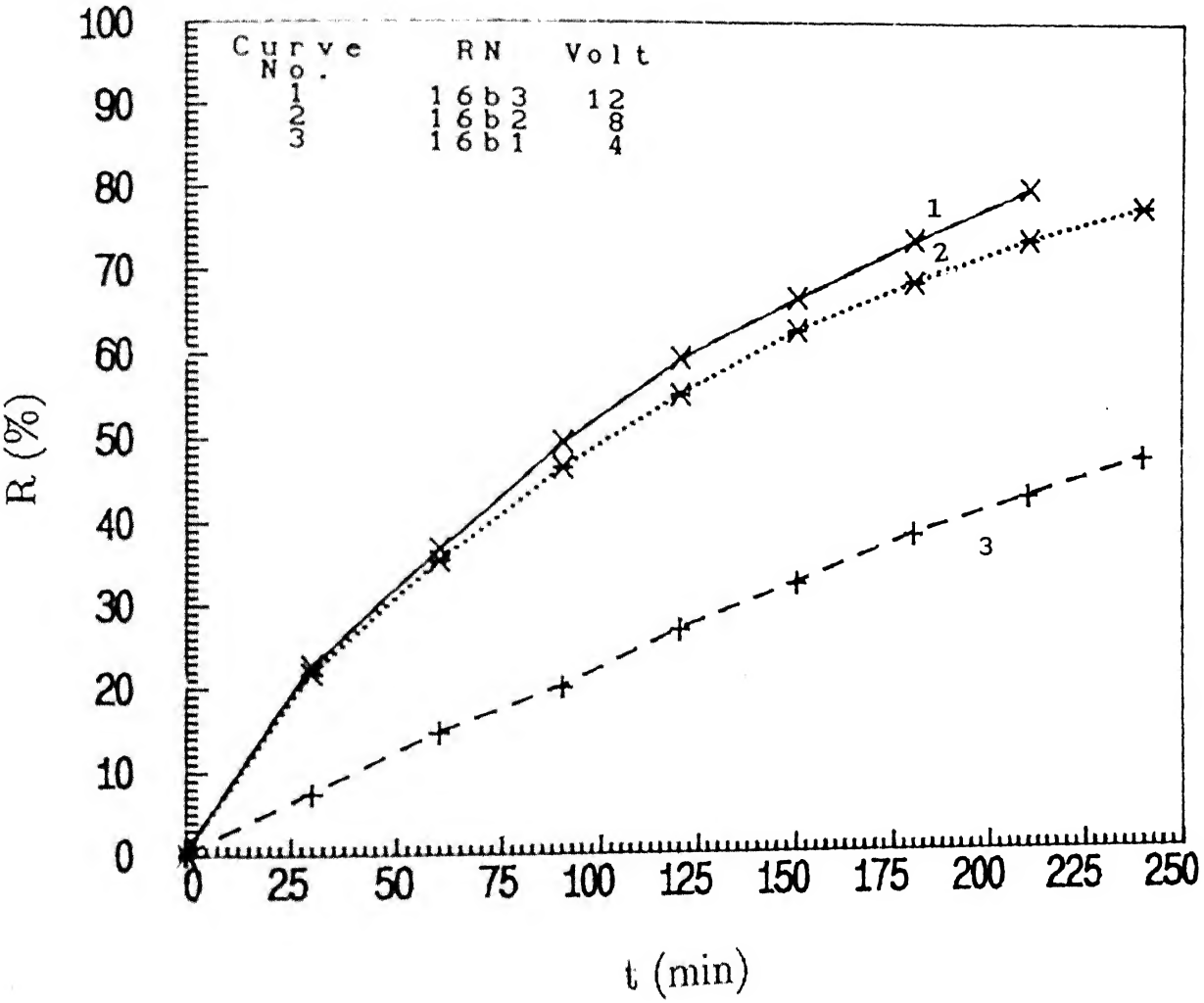


Fig. 4.17 Effect of voltage on percent removal

Flow rates (ml/min)		Concentration (mol/l)	
Feed	130	Feed (Ca^{2+})	0.025
Catholyte	830	Catholyte (EDTA)	0.025
Anolyte	830	(AA)	0.025

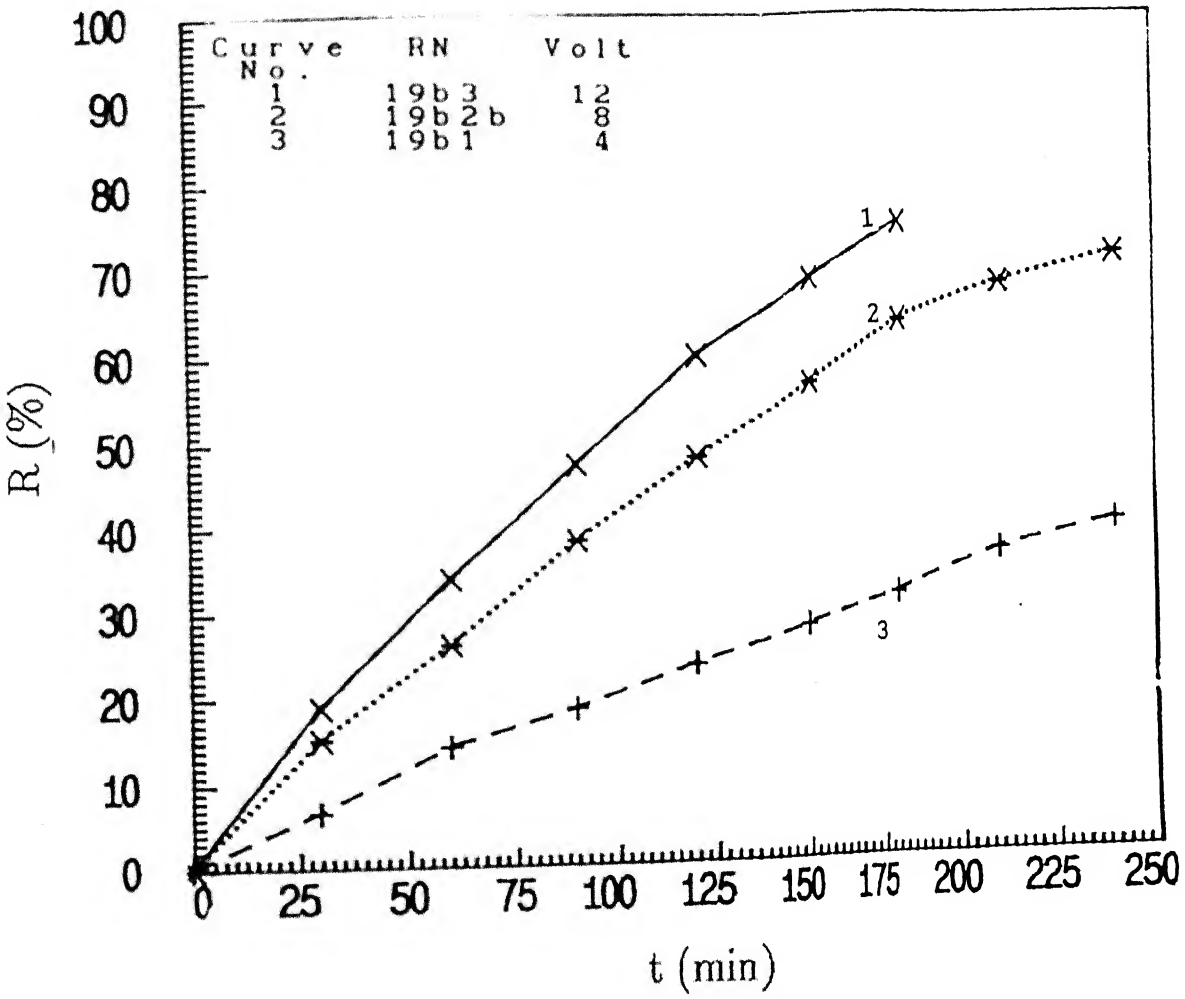


Fig. 4.18 Effect of voltage on percent removal

Flow rates (ml/min)		Concentration (mol/l)	
Feed	130	Feed (Ca^{2+})	0.05
Catholyte	830	Catholyte (EDTA)	0.05
Anolyte	830		0.05

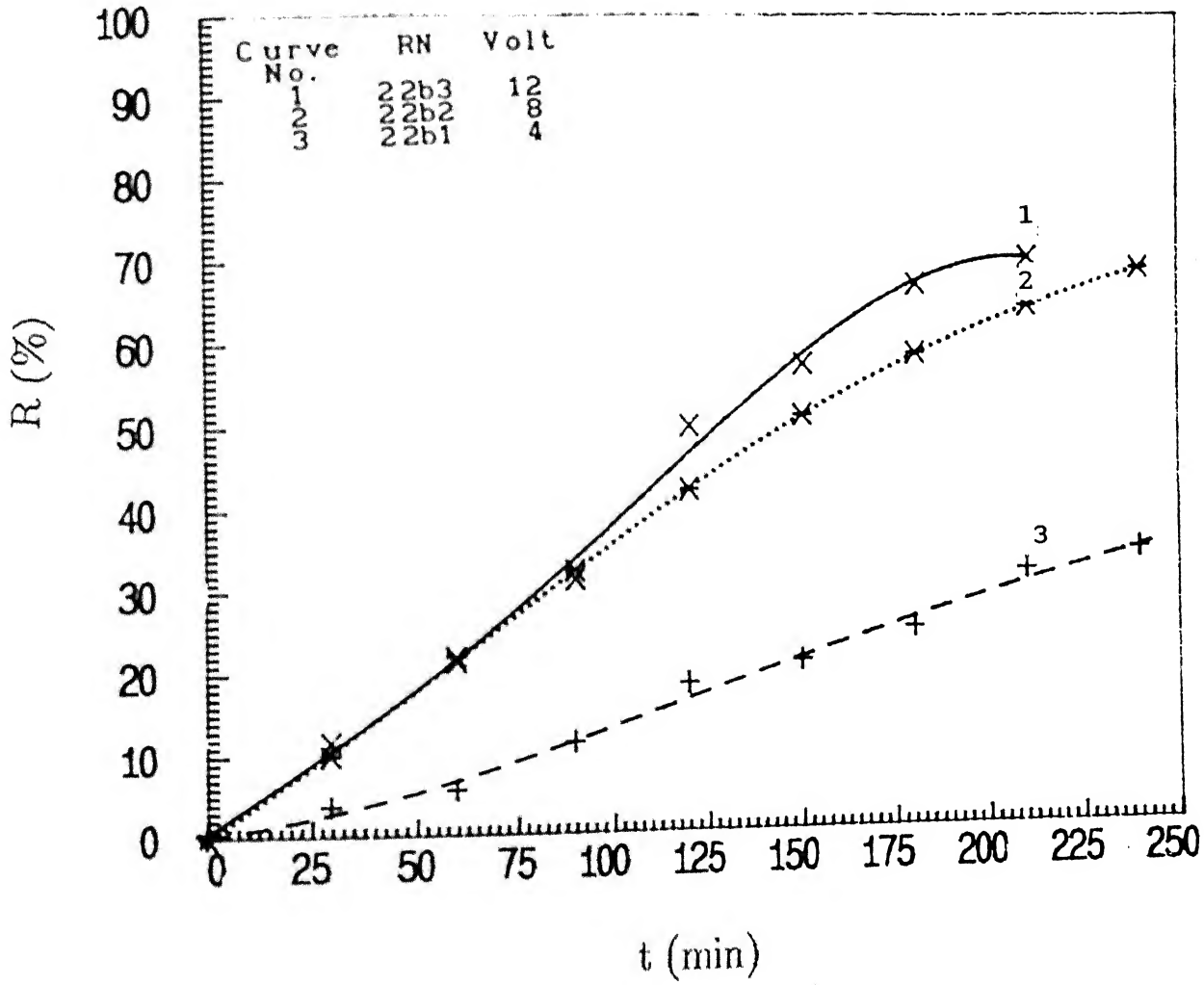


Fig. 4.19 Effect of voltage on percent removal

Flow rates (ml/min)	
Feed	130
Catholyte	830
Anolyte	830

Concentration (mol/l)	
Feed (Ca^{2+})	0.075
Catholyte (EDTA)	0.075
Catholyte (AA)	0.075

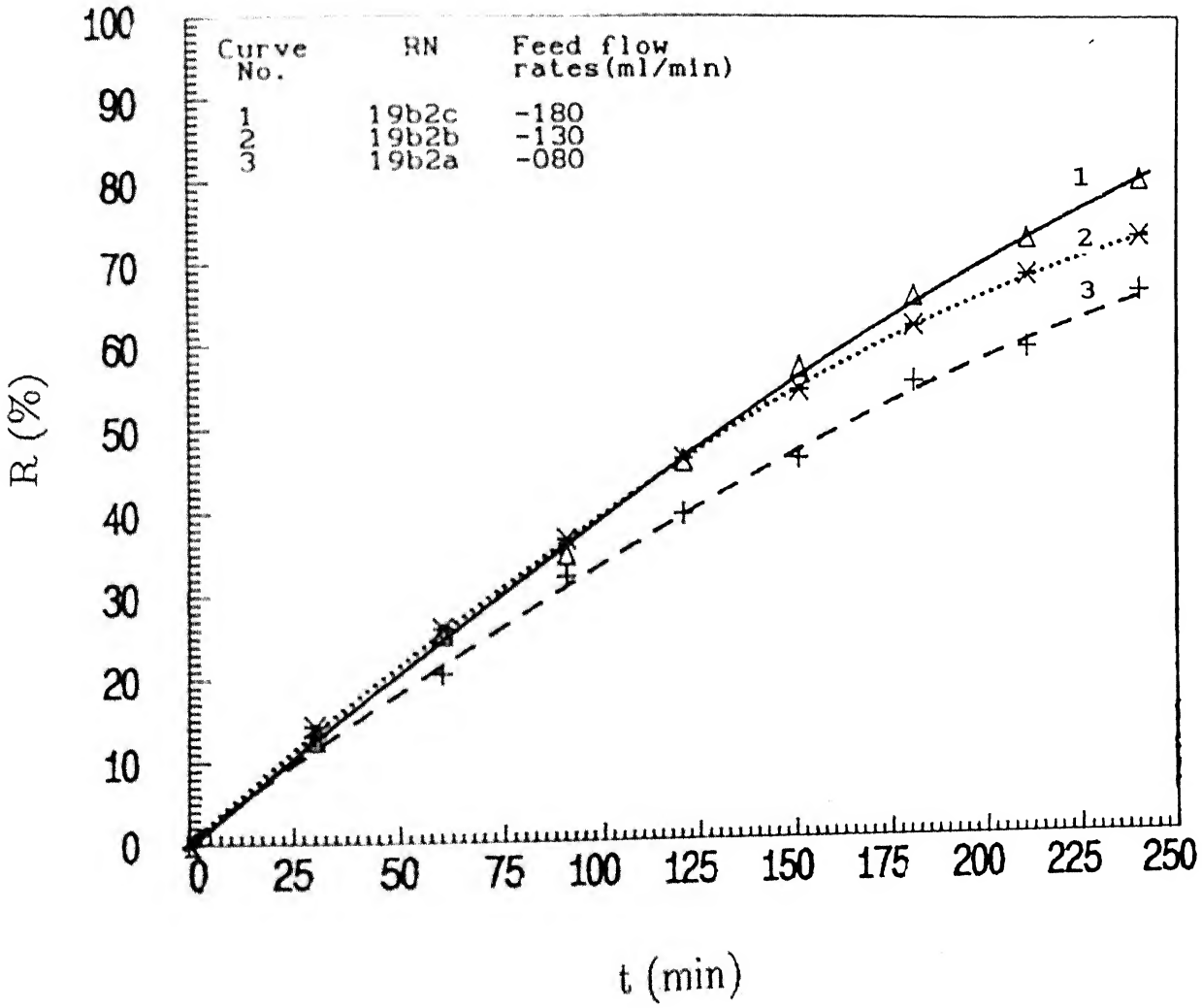


Fig. 4.20 Effect of feed flow rate on percent removal

Flow rates(ml/min)		Concentration(mol/l)	
Feed	varied		
Catholyte	830	Feed(Ca^{2+})	0.05
Anolyte	830	Catholyte EDTA	0.05
		Catholyte AA	0.05
Voltage - 8 V			

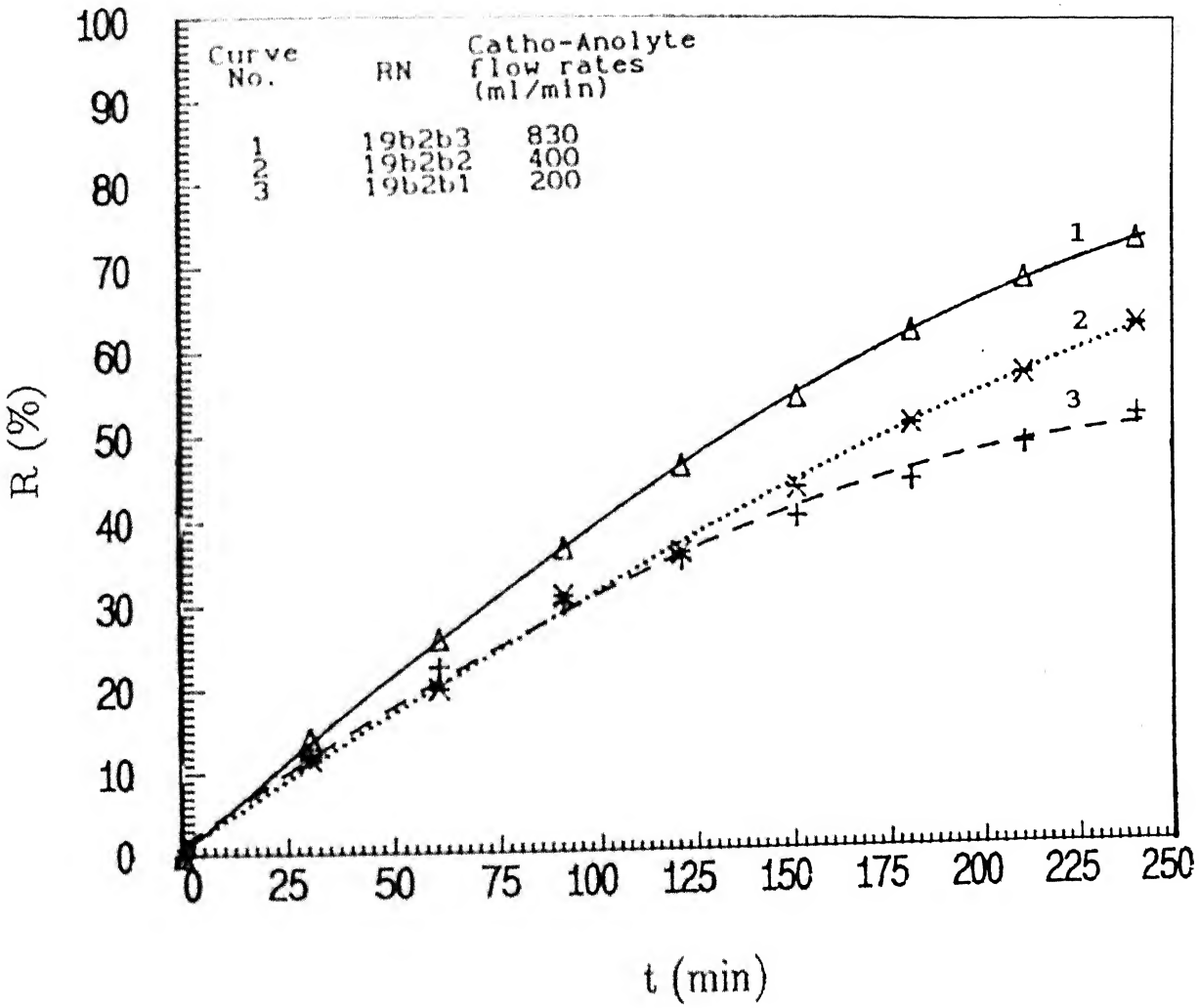


Fig. 4.21 Effect of catholyte-anolyte flow rate on percent removal

Flow rates (ml/min)		Concentration (mol/l)	
Feed	130	Feed (Ca^{2+})	0.05
Catholyte / Anolyte	} Varied	Catho- EDTA	0.05
		lyte AA	0.05
Voltage - 8.0 V			

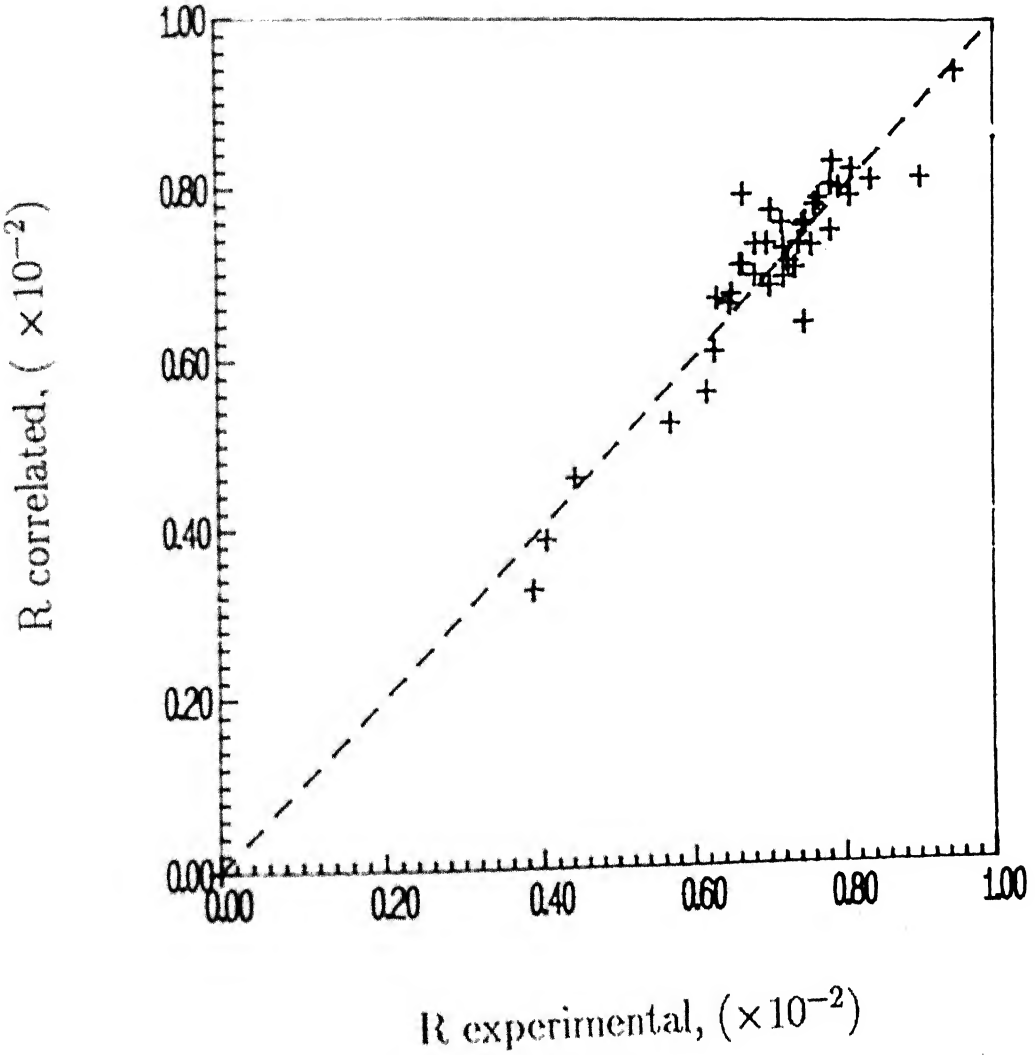


Fig. 4.22 Comparison between correlated and experimentally obtained values of removal

CHAPTER 5

Conclusions

Electrodialytic removal of calcium from synthetic sugar solution showed encouraging esults. A new technique has been found out, the best probable system has been chosen, nd the parametric variation of this system is done. The following conclusions are drawn rom the experimental results:

1 A large variety of combinations of catholyte streams were tried, namely, distilled water, alkali (NaOH), acetic acid and EDTA. The anolyte stream was tried only with distilled water and a dilute HCl solution.

2 Fouling of the cation exchange membrane was minimum when the catholyte consisted of an aqueous solution of EDTA and acetic acid.

3 The purpose of Acetic acid in the catholyte stream is primarily the maintenance of an acidic pH in that chamber.

4 The feed flow direction should be counter current to that of the catholyte and anolyte streams in order to maintain a constant driving force.

5 To achieve better percent removal of calcium, the feed flow rate should have an optimum value. It should not be very high so that pumping costs and heating up of the system, i.e. energy losses are minimum.

6 The catholyte and anolyte flow rates should be 3-4 times higher than the feed flow rate for most efficient operation.

7 With an increase of applied voltage the percent removal increased but an optimum voltage is to be used to avoid unusual wastage of power and over heating of the system.

Recommendations

1 Detailed experimental analysis can be carried out by further changing the catholyte and anolyte composition.

2 It is better to use a lower concentration of acid in the anolyte chamber or an alkaline solution may also be used. This will neutralize the acidic effect of Cl_2 in aqueous medium.

3 Mathematical modeling can be done to predict fouling and other physico–chemical phenomena involved in the process by taking into consideration the extensive experimental analysis presented here.

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APPENDIX

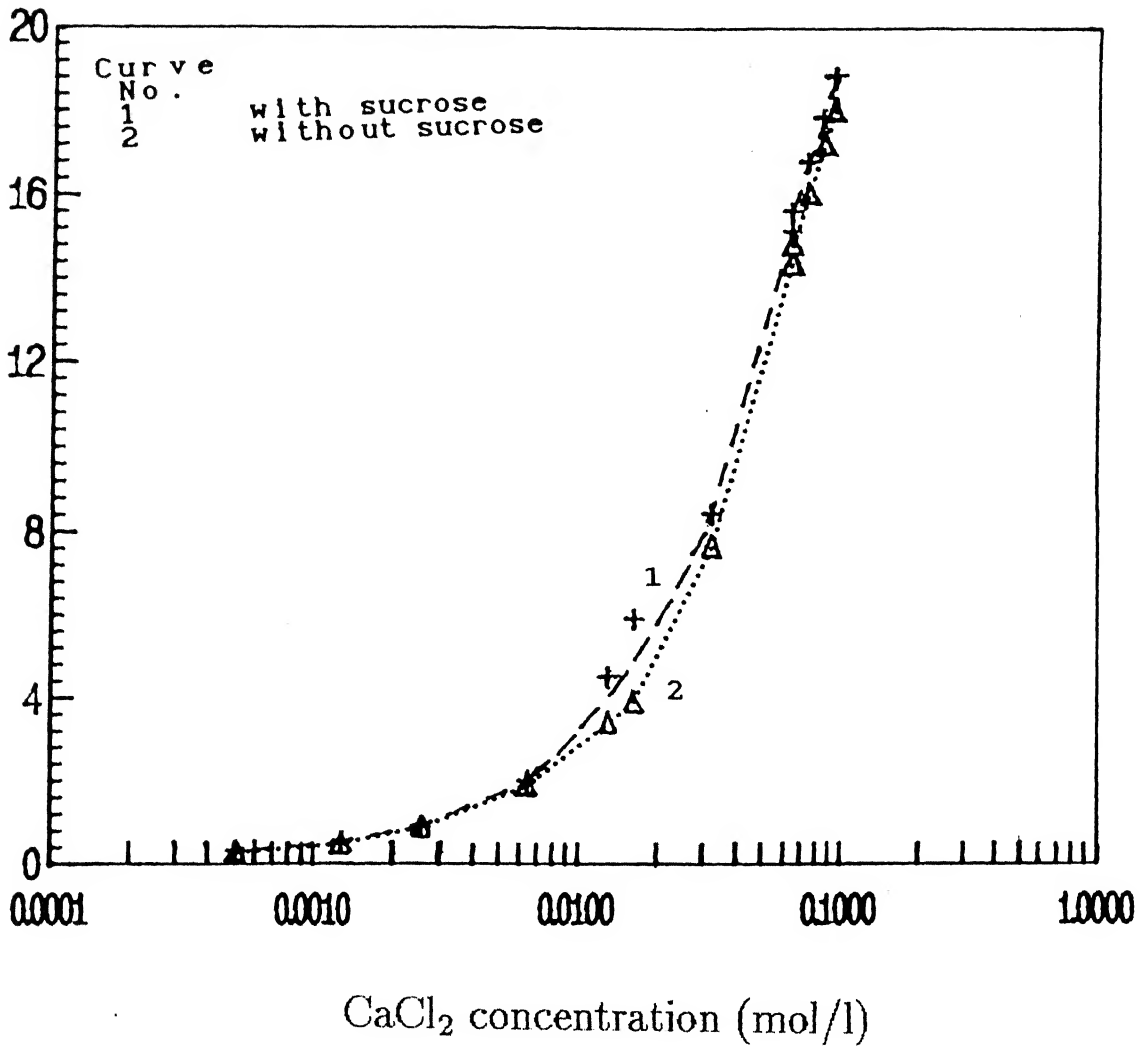

Fig. A.1 Calibration curve for $CaCl_2$ with and without sucrose

APPENDIX - A

RN=A1 A=W, C=W, V=2.0							
t	0	20	30				
I	0.01	0.01	0.01				
λ	5.9	5.9	5.9				
R	0	0.0	0.0				
Obs= no separation							
RN=A2 A=W, C=W, and V=4.0							
t	0	20	50	80	110	140	165
I	0.01	0.07	0.14	0.17	0.19	0.20	0.18
λ	5.9	5.8	5.6	5.3	5.2	4.8	4.7
R	0.0	1.7	5.1	10.2	11.8	18.6	20.3
Obs= Separation is Possible.							
RN=A3 A=0.02 M HCl, C=0.02 M NaOH, V=4.0							
t	0.0	20	30	60	80		
I	0.30	0.20	0.18	0.14	0.12		
λ	5.8	5.6	5.4	5.0	5.0		
R	-	3.4	6.9	13.8	13.8		
Obs= f and AW was done							
RN=1 Table 1.1 A=0.1 M HCl, C=0.1 M NaOH, V=4.0							
t	0.0	20	30	50	60	70	
I	0.68	0.31	0.29	0.28	0.27	0.26	
λ	5.9	5.5	5.4	5.2	5.2	5.0	
R	-	1.7	6.8	8.5	11.8	15.25	
Obs= f, acid wash (AW) done on the CEM for 3 mins and all the catholyte, feed and anolyte left were used in the next table.							
Table 1.2							
4t	00	20	30	50	60	70	
I	0.5	-	0.28	0.25	0.24	0.22	
λ	5.0	-	4.5	4.2	4.2	4.1	
R	-	10.0	16.0	16.0	18.0		
Obs= f, after acid wash(AW) on CEM the feed, catholyte and anolyte solutions left were used in ED							

Table 1.3			
t	00	15	20
I	0.49	0.29	0.29
λ	4.1	3.9	3.8
R	00	4.9	7.3
Obs= f, After AW a fresh solution of A and C were used for the next table.			

Table 1.4			
t	00	15	30
I	0.57	0.28	0.26
λ	3.8	3.4	3.1
R	00	10.5	18.4
Obs= f, AW was done for 4 mins and the next run followed.			

Table 1.5				
t	00	15	30	45
I	0.43	0.25	0.24	0.22
λ	3.1	3.0	2.9	2.8
R	00	3.2	6.4	9.7
Obs= f, A.W. was done for 15 mins. and the next run followed.C solution pH=12.56				

Table 1.6			
t	00	15	30
I	0.37	0.23	0.22
λ	2.8	2.6	2.5
R	00	7.1	10.7
Obs= f, AW was done for 5 mins. and used in the run.			

Table 1.7				
t	00	15	30	45
I	0.25	0.21	0.20	0.20
λ	2.5	2.4	2.2	2.0
R	00	4.0	12.0	20.0
Obs= f, AW was done and next run followed.				

Table 1.8				
t	00	15	30	45
I	0.40	0.17	0.16	0.16
λ	2.0	1.96	1.88	1.78
R	00	5.6	11.2	17.4
Obs= f, AW was done and next run followed.				

Table 1.9

t	00	15	30	45	60	75	90	105
I	0.28	0.15	0.14	0.13	0.12	0.12	0.11	0.11
λ	1.78	1.68	1.58	1.47	1.39	1.32	1.26	1.22
R	00	5.6	11.2	17.4	21.9	25.8	29.2	31.8

Obs= f, AW was done and next run followed.

Table 1.10

t	00	15	30	45	60
I	0.21	0.11	0.09	0.08	0.07
λ	1.22	1.16	1.10	1.04	0.98
R	00	4.9	9.8	14.7	19.7

Obs= f, AW was done and next run followed.

Table 1.11

t	00	15	30	45	55
I	0.20	0.14	0.06	0.05	0.05
λ	0.98	0.89	0.86	0.84	0.79
R	00	9.2	12.2	14.3	19.40

Due to power cut at 55 mins. the system turned off and the later observations are tabulated here under this section.

t	00	15	45	60	75	90
I	0.12	0.05	0.04	0.04	0.03	0.03
λ	0.79	0.72	0.62	0.58	0.52	0.51
R	00	8.8	21.5	26.6	34.0	35.4

At the end of total 665 mins the percent removal observed was 91.35.

RN= 2a

A=W, C=0.025 M EDTA, V=4.0

R.I. of the F solution at the begining was 1.338

R.I. of the F solution at the end was 1.3375

So almost no change in R.I.(no sucrose transfer).

t	00	20	40	60	80	100	130	160	190	230
I	.01	.03	.12	.20	.24	.26	.26	.27	.26	0.25
λ	5.9	5.8	5.6	5.5	5.4	5.3	4.8	4.3	4.0	3.6
R	00	1.7	5.1	6.8	8.5	10.2	18.6	27.1	32.2	38.9
t	250	280	310	340	370	400	430	460	490	
I	.23	.25	.23	.21	.19	.18	.17	.15	.13	
λ	3.5	3.1	2.9	2.5	2.2	2.1	1.80	1.56	1.42	
R	40.7	47.5	50.8	57.6	62.7	64.4	69.5	71.86	75.93	
t	520	550	580	610						
I	.12	.09	.07	.06						
λ	1.26	1.10	1.00	0.98						
R	78.6	81.35	83.5	83.5						

Obs=f on CEM, the CEM was washed with dilute acid and used in the next run.

RN= 2b

A=W, C=0.05 M EDTA, V=4.0

t	00	15	30	45	60	90	125
I	0.04	0.13	0.20	0.26	0.31	0.27	0.24
λ	4.5	-	4.3	-	4.0	3.6	3.2
R	00	4.4	11.1	20.0	28.8		

Obs=nf on CEM . The rate increased. The same CEM and AEM were used in the next run.

RN=3

A=0.1 M HCl, C=0.05 M EDTA(pH=4.2), V=4.0

t	00	30	60	90	120	150	180	210	240	265
I	.60	.35	.32	.30	.28	.26	.23	.22	.20	.18
λ	5.8	5.2	4.8	4.2	4.0	3.5	3.2	2.7	2.4	2.1
R	00	10.3	17.2	27.6	31.0	39.6	44.8	53.4	58.6	63.8

Obs=nf.

RN=4

A=0.1 M HCl, C=0.025 M EDTA(pH=4.4), V=4.0

t	00	30	60	90	120	150	210	240	270	300
I	.40	.32	.33	.31	.29	.28	.23	.22	.20	.19
λ	6.6	6.1	5.9	5.4	5.0	4.7	4.1	3.7	3.5	3.1
R	00	7.6	10.6	18.2	24.0	28.8	37.9	43.9	46.9	51.1

Obs= Slight fouling was observed on the CEM and used for the next run after cleaning.

RN=5

A=0.1 M HCl, C=0.025 M EDTA + NaOH(pH=6.53), V=4.0

t	00	30	60	90	120	150	240	270	300
I	.57	.38	.35	.33	.31	.29	.23	.21	.19
λ	6.5	6.1	5.7	5.4	5.0	4.6	3.8	3.5	3.4
R	-	6.2	12.3	16.9	23.1	29.2	41.5	46.2	47.7

Obs=f on CEM and it was totally removed by dilute acid wash.

RN=6

A=0.1 M HCl, C=0.025 M EDTA + NaOH(pH=9.81), V=4.0

t	00	30	60	90	120	150	210	270	300
I	.52	.37	.34	.31	.28	.25	.21	.18	.16
λ	5.7	5.1	4.8	4.4	4.0	3.4	2.7	2.3	2.0
R	-	10.5	15.8	22.8	29.8	40.3	52.6	59.6	65.1

Obs=f occured on CEM and it was totally removed by dilute acid wash.

RN=7

A=0.1 M HCl, C=0.025 M EDTA + NaOH(pH=12.18), V=4.0

t	00	30	60	90	120	150	180	210	240
I	.62	.41	.37	.33	.28	.26	.23	.21	.18
λ	6.1	5.4	4.8	4.6	4.4	4.0	3.6	3.5	3.1
R	-	11.5	21.1	24.6	27.9	34.4	40.9	42.67	49.2

Obs=f observed on CEM and washed with dilute acid wash.

RN=8

A=0.1 M HCl, C=0.05 M AA(pH=2.96), V=4.0

t	00	30	70	95	135	150	180	210	240	270
I	.13	.06	.11	.13	.21	.22	.24	.25	.25	.24
λ	6.2	6.1	5.9	5.8	5.3	5.2	4.9	4.5	4.2	3.7
R	-	1.6	4.8	6.5	14.5	16.1	20.9	27.4	32.3	40.3
t	300	330	360	390	420	450				
I	.22	.21	.19	.18	.16	.15				
λ	3.1	2.9	2.6	2.3	2.0	1.9				
R	50.0	51.6	58.1	62.9	67.7	69.35				

Obs=nf on either of cation or anion exchange membrane. The current reaches maximum and then decreased;this probably due to initially the catholyte chamber resistance was high due to very weak feably dissociating acetic acid; but with time due to entry of calcium ions it started ionising leading there by increase in current value. But the middle feed chamber resistance is always decreasing so when is played more important role the overall cell resistance again started increasing showing a decreasing in current value.

RN=9

A=0.1 M HCl, C=0.025 M EDTA + 0.05 M AA(pH=3.51), V=4.0

t	00	30	60	90	120	150	180	210	240	270	300
I	.49	.45	.44	.41	.38	.36	.32	.30	.27	.25	.22
λ	7.5	6.8	6.2	5.6	5.1	4.7	4.3	3.8	3.3	2.9	2.7
R	-	9.3	20.0	25.3	32.0	37.3	42.7	49.3	56.0	61.3	64.0
t	330	360	390	420	450	480	510	540	570		
I	.21	.18	.17	.16	.14	.12	.11	.08	.05		
λ	2.3	2.1	1.9	1.69	1.51	1.27	1.11	0.93	0.83		
R	69.3	72.0	74.7	77.5	79.9	83.1	85.2	87.6	88.9		

RN=10

A=0.1 M HCl, C=0.025 M EDTA(pH=4.4), V=8.0

t	00	30	60	90	120	150	180	210	270	345
I	.91	.65	.60	.53	.47	.41	.35	.31	.24	.18
λ	5.4	4.9	4.4	3.8	3.2	2.8	2.3	1.9	1.51	0.95
R	-	9.3	18.52	29.6	40.7	48.2	57.4	64.8	72.0	82.4

Obs=f slightly on the CEM which was perfectly cleaned with dilute acid wash.

RN=11

A=0.1 M HCl, C=0.025 M EDTA + NaOH(pH=9.86), V=8.0

t	00	30	60	90	120	150	180	210	240	270	300
I	1.2	.85	.51	.43	.36	.28	.25	.22	.20	.18	.10
λ	6.1	4.6	3.9	3.2	2.8	2.3	2.0	1.77	1.54	1.26	0.98
R	-	24.6	36.1	47.5	54.1	62.3	67.2	71.0	74.7	79.3	83.9

Obs=f on the CEM and the membrane was perfectly cleaned with dilute acid wash.

RN=12

A=0.1 M HCl, C=0.025 M EDTA + 0.05 M AA(pH=3.47), V=8.0

t	00	30	60	90	120	150	180	210	240	270	300
I	1.02	.75	.59	.51	.44	.38	.32	.27	.23	.20	.18
λ	6.1	5.1	4.3	3.7	3.1	2.7	2.3	2.0	1.8	1.6	1.5
R	0.0	16.7	29.8	39.4	49.5	56.0	61.6	67.12	70.5	73.7	75.5

Feed flow is counter current to the Catholyte and Anolyte flow

RN =13

A=0.1 M HCl, C=0.025 M EDTA + 0.05 M AA(pH=3.47), V=8.0

t	00	30	60	90	120	150	180	225
I	1.02	0.87	0.74	0.57	0.48	0.37	0.30	0.22
λ	6.2	4.7	3.8	3.2	2.6	2.2	1.8	1.4
R	0.0	24.8	38.76	48.7	57.2	64.9	71.23	76.7

APPENDIX - C

RN=14a, α=0.48365, β=0.91406									
t	00	30	65	90	120	150	180	210	240
I	.44	.42	.42	.63	.65	.54	.44	.35	.29
λ	6.5	5.4	4.9	4.3	3.5	3.0	2.7	2.4	1.98
R	-	10.5	19.9	29.6	42.1	50.9	56.1	61.1	67.5
RN=14b, α=0.70702, β=0.8501									
t	00	30	60	90	120	150	180	210	240
I	.50	.53	.54	.56	.53	.47	.37	.33	.27
λ	6.3	5.3	4.7	4.0	3.5	3.0	2.5	2.0	1.73
R	-	12.4	22.9	33.6	41.9	50.8	58.7	66.5	71.6
RN=14c, α=1.20354, β=0.75872									
t	00	30	60	90	120	150	180	210	240
I	.55	.56	.58	.57	.54	.50	.45	.40	.34
λ	6.7	5.1	4.4	3.9	3.3	2.7	2.2	1.92	1.47
R	-	15.9	26.8	35.8	46.3	55.2	62.7	68.5	75.8
RN=14d, α=1.59913, β=0.71055									
t	00	30	60	90	120	150	180	210	240
I	.55	.57	.61	.60	.53	.49	.40	.33	.28
λ	6.7	5.0	4.3	3.6	3.2	2.6	2.3	2.2	1.76
R	-	17.9	28.9	39.8	47.8	57.2	64.0	71.1	77.8
RN=15b, α=0.77003, β=0.84686									
t	00	30	60	90	120	150	180	210	240
I	.69	.65	.62	.54	.54	.47	.38	.30	.25
λ	6.4	5.3	4.5	3.8	3.3	2.7	2.3	1.89	1.71
R	-	12.5	26.6	37.5	45.3	54.7	62.5	69.0	71.9
RN=15c, α=1.41462, β=0.74227									
t	00	30	60	90	120	150	180	210	240
I	.78	.74	.68	.59	.50	.46	.34	.28	.22
λ	6.6	5.0	4.4	3.5	2.9	2.4	2.0	1.68	1.41
R	-	17.2	28.1	42.6	52.5	60.4	67.0	72.3	76.9

RN=15d, α=1.992579, β=0.68191									
t	00	30	60	90	120	150	180	210	240
I	.77	.73	.70	.63	.53	.45	.36	.28	.24
λ	6.4	4.9	4.2	3.3	2.7	2.3	1.83	1.51	1.33
R	-	19.9	30.9	45.4	55.0	62.2	69.9	75.3	78.1
RN=16a, α=1.2662, β=0.7445									
t	00	30	60	90	120	150	180	210	240
I	0.96	0.83	0.73	0.62	-	-	0.37	0.28	0.24
λ	6.6	5.6	4.8	4.1	3.4	3.0	2.6	2.3	2.0
R	0.0	14.92	27.31	37.74	47.50	54.83	60.50	65.34	69.77
RN=16b1, α=0.3556, β=0.89766									
t	00	30	60	90	120	150	180	210	240
I	0.39	0.39	0.38	0.38	0.38	0.37	0.36	0.35	0.34
λ	6.8	6.3	5.8	5.4	5.0	4.6	4.2	3.9	3.6
R	0.0	7.30	14.54	19.97	26.85	32.30	38.20	42.65	47.09
RN=16b2, α=2.7907, β=0.61502									
t	00	30	60	90	120	150	180	210	240
I	1.05	0.89	0.79	0.67	0.57	0.47	0.37	0.32	0.24
λ	6.7	5.2	4.4	3.6	3.0	2.5	2.1	1.8	1.53
R	0.0	21.6	34.3	46.3	54.9	62.34	68.16	73.23	77.15
RN=16b3, α=2.533, β=0.6509									
t	00	30	60	90	120	150	180	210	
I	1.66	1.29	1.12	0.90	0.68	0.53	0.42	0.34	
λ	7.1	5.5	4.5	3.6	2.9	2.4	1.9	1.46	
R	0.00	22.50	36.60	49.30	59.10	66.20	73.19	79.42	
RN =16c, α=3.70617, β=0.56813									
t	00	30	60	90	120	150	180	225	
I	1.02	0.87	0.74	0.57	0.48	0.37	0.30	0.22	
λ	6.2	4.7	3.8	3.2	2.6	2.2	1.8	1.4	
R	0.0	24.8	38.76	48.7	57.2	64.9	71.23	76.7	
RN=16d, α=2.86738, β=0.61977									
t	00	30	60	90	120	150	180	210	240
I	1.2	0.87	0.78	0.65	0.54	0.44	0.35	0.29	0.25
λ	6.5	5.0	4.1	3.4	2.7	2.2	1.75	1.43	1.3
R	0.0	22.98	36.79	48.02	57.83	66.54	72.96	77.99	80.31
RN=17a, α=1.7052, β=0.70097									
t	00	30	60	90	120	150	180	210	240
I	1.16	0.88	0.76	0.64	0.55	0.43	0.36	0.34	0.22
λ	6.6	5.5	4.5	3.7	3.1	2.7	2.3	2.0	1.8
R	0.0	16.70	31.81	42.94	53.06	59.1	64.60	69.23	72.6
RN=17b, α=3.99802, β=0.56044									
t	00	30	60	90	120	150	180	210	240
I	1.28	0.95	0.79	0.64	0.53	0.41	0.31	0.26	0.21
λ	6.6	4.8	3.9	3.2	2.6	2.1	1.8	1.3	1.1
R	0.0	26.24	39.88	50.96	59.64	67.62	73.14	79.56	83.41

RN=17c, α=2.2727, β=0.65529									
t	00	30	60	90	120	150	180	210	240
I	1.19	0.95	0.80	0.67	0.53	0.43	.38	.33	.29
λ	6.6	5.3	4.3	3.5	3.0	2.5	2.1	1.7	1.4
R	0.0	19.72	34.51	45.94	54.87	61.25	68.20	73.50	78.03
RN=17d, α=3.0207, β=0.60724									
t	00	30	60	90	120	150	180	210	240
I	1.32	1.13	0.89	0.75	0.59	0.48	0.39	0.32	0.27
λ	7.0	5.4	4.4	3.6	3.0	2.5	2.0	1.7	1.3
R	0.0	22.86	36.67	48.57	57.14	64.28	71.0	75.76	80.85
RN=18a, α=0.46583, β=0.91877									
t	00	30	60	90	120	150	180	210	240
I	1.24	1.19	1.18	1.13	1.10	0.94	0.75	0.63	0.53
λ	11.9	10.7	9.5	8.3	7.1	6.0	5.1	4.6	4.2
R	0.0	10.00	20.17	30.25	40.33	49.01	57.00	61.50	64.30
RN=18b, α=1.1774, β=0.76307									
t	00	30	60	90	120	150	180	210	240
I	1.22	1.16	1.16	1.16	1.10	1.02	0.93	0.81	0.66
λ	11.9	10.1	8.8	7.3	6.2	5.1	4.3	3.8	3.4
R	0.0	15.21	26.17	38.25	47.96	56.43	63.34	67.73	71.03
RN=18c, α=1.3234, β=0.75108									
t	00	30	60	90	120	150	180	240	
I	1.39	1.32	-	-	1.17	0.96	0.83	0.59	
λ	11.6	9.7	8.3	6.7	5.8	4.7	3.6	3.1	
R	0.0	16.55	28.22	39.88	49.96	59.04	68.72	73.34	
RN=19a, α=0.52966, β=0.90429									
t	00	30	60	90	120	150	180	210	240
I	1.64	1.51	1.41	1.29	1.13	0.95	0.83	0.65	0.53
λ	11.7	10.8	9.3	8.1	6.9	5.9	5.0	4.1	3.7
R	0.00	10.50	22.57	33.04	42.44	51.13	58.18	64.81	68.57
RN=19b1, α=0.43554, β=0.82796									
t	00	30	60	90	120	150	180	210	240
I	0.59	0.59	0.60	0.61	0.63	0.60	0.59	0.58	0.57
λ	11.9	11.1	10.2	9.7	9.1	8.6	8.2	7.6	7.2
R	0.00	06.7	14.30	18.50	23.50	27.70	31.10	36.13	39.50
RN=19b2a, α=0.855, β=0.79719									
t	00	30	60	90	120	150	180	210	240
I	1.40	1.38	1.34	1.26	1.15	1.03	0.88	0.78	0.71
λ	12.1	10.5	9.6	8.2	7.3	6.5	5.4	4.9	4.0
R	0.00	13.22	20.66	32.23	39.67	46.28	55.37	59.5	66.94

RN=19b2b or 19b2b3, α=1.006, β=0.7922									
t	00	30	60	90	120	150	180	210	240
I	1.69	1.49	1.46	1.39	1.22	1.13	0.95	0.74	0.63
λ	12.7	10.3	8.9	7.6	6.4	5.5	4.6	3.8	3.2
R	0.00	14.32	26.05	36.71	46.53	54.39	62.20	68.50	73.23
RN=19b2b1, α=1.3276, β=0.67877									
t	00	30	60	90	120	150	180	210	240
I	1.54	1.40	1.35	1.24	1.14	0.98	0.88	0.80	0.72
λ	11.9	10.4	9.2	8.3	7.7	7.1	6.6	6.1	5.7
R	0.00	12.30	22.70	30.20	35.29	40.30	44.50	48.70	52.10
RN=19b2b2, α=0.74868, β=0.81201									
t	00	30	60	90	120	150	180	210	240
I	1.58	1.32	1.26	1.17	1.04	0.94	0.80	0.70	0.59
λ	11.9	10.5	9.5	8.2	7.6	6.7	5.8	5.1	4.4
R	0.00	11.76	20.10	31.10	36.10	43.67	51.26	57.14	63.02
RN=19b2c, α=0.6418, β=0.889									
t	00	30	60	90	120	150	180	210	240
I	1.71	1.66	1.61	1.55	1.35	1.15	0.89	0.72	0.55
λ	12.6	11.0	9.4	8.2	6.8	5.4	4.3	3.4	2.5
R	0.00	12.70	25.40	34.90	46.00	57.11	65.90	73.0	83.16
RN=19b3, α=1.357, β=0.76307									
t	00	30	60	90	120	150	180		
I	2.71	2.48	2.18	1.79	1.39	1.03	0.72		
λ	12.7	10.3	8.4	6.7	5.1	4.0	3.2		
R	0.00	18.89	33.86	47.24	59.84	68.50	74.80		
RN=19c, α=1.14756, β=0.77385									
t	00	30	60	90	120	150	180	210	240
I	1.62	1.48	1.42	1.29	1.17	0.94	0.78	0.62	0.53
λ	12.1	10.3	8.6	7.5	6.2	5.2	4.1	3.6	3.0
R	0.00	15.09	28.31	38.28	48.22	56.78	65.77	70.02	74.55
RN=20a, α=0.9487, β=0.79286									
t	00	30	60	90	120	150	180	210	240
I	1.80	1.47	1.37	1.24	1.06	0.88	0.69	0.53	0.44
λ	12.1	10.5	9.4	8.0	6.7	5.8	5.1	4.5	4.0
R	0.00	14.00	23.14	34.72	44.63	51.89	58.12	62.92	67.04
RN=20b, α=1.56469, β=0.7093									
t	00	30	60	90	120	150	180	210	240
I	2.22	1.82	1.48	1.08	0.77	0.65	0.65	0.48	0.42
λ	11.9	10.1	8.8	7.5	6.3	5.5	4.7	4.2	3.6
R	0.00	17.44	28.01	38.65	47.90	54.94	61.53	65.75	70.03

RN=20c, α=2.0385, β=0.66205									
t	00	30	60	90	120	150	180	210	240
I	1.93	1.59	1.37	1.06	0.66	0.51	0.47	0.42	0.38
λ	12.2	9.7	8.6	7.5	6.1	5.1	4.6	4.0	3.5
R	0.00	20.00	29.74	38.05	49.67	57.88	62.51	66.92	71.00
RN=21a, α=0.42935, β=0.89959									
t	00	30	60	90	120	150	180	210	240
I	1.53	1.58	1.69	1.61	1.28	0.86	0.65	0.54	0.46
λ	16.0	14.6	13.3	11.8	10.6	9.6	8.6	7.7	7.1
R	0.00	08.75	16.87	26.25	33.51	40.06	46.12	51.55	55.43
RN=21b, α=0.438, β=0.92706									
t	00	30	60	90	120	150	180	210	240
I	1.68	1.73	1.79	1.80	1.75	1.65	1.50	1.24	0.95
λ	16.7	14.4	12.7	11.5	09.6	08.1	7.2	6.3	5.9
R	0.00	09.58	20.36	28.14	40.12	49.10	55.01	60.54	63.24
RN=22a, α=0.6578, β=0.85382									
t	00	30	60	90	120	150	180		
I	2.02	2.12	2.02	1.88	1.68	1.46	1.20		
λ	16.0	14.0	12.8	11.10	09.5	8.3	7.2		
R	0.00	12.50	20.00	30.62	40.62	48.23	54.86		
RN=22b1, α=0.0716, β=1.1303									
t	00	30	60	90	120	150	180	210	240
I	0.82	0.82	0.82	0.82	0.82	0.82	0.81	0.81	0.81
λ	15.8	15.2	14.9	14.0	12.90	12.5	11.90	10.80	10.40
R	0.00	03.80	05.70	11.40	18.35	20.90	24.70	31.64	34.07
RN=22b2, α=0.48185, β=0.92173									
t	00	30	60	90	120	150	180	210	240
I	2.25	2.29	2.28	2.18	1.93	1.64	1.33	1.07	0.81
λ	17.2	15.4	13.4	11.6	9.9	8.4	7.2	6.2	5.4
R	0.00	10.10	22.10	32.46	42.18	51.0	58.31	64.0	68.52
RN=22b3, α=0.4323, β=0.96679									
t	00	30	60	90	120	150	180	210	
I	3.50	3.30	3.00	2.41	1.84	1.41	1.02	0.75	
λ	16.2	14.3	12.70	11.1	8.1	6.90	5.40	4.86	
R	0.00	11.80	21.50	31.40	49.90	57.20	66.80	70.00	
RN=22c, α=1.4562, β=0.71414									
t	00	30	60	90	120	150	180	210	240
I	2.10	2.15	2.07	1.96	1.78	1.59	1.31	1.05	0.81
λ	16.1	13.30	12.10	10.5	8.7	7.3	6.1	5.3	4.8
R	0.00	17.40	24.84	34.96	45.62	54.17	61.73	67.04	69.95